US012235232B2

(12) **United States Patent**
Ito et al.

(10) **Patent No.: US 12,235,232 B2**
(45) **Date of Patent: Feb. 25, 2025**

(54) **GAS SENSOR, METHOD OF MANUFACTURING GAS SENSOR, AND FUEL CELL VEHICLE**

(71) Applicant: **Nuvoton Technology Corporation Japan**, Kyoto (JP)

(72) Inventors: **Satoru Ito**, Hyogo (JP); **Kazunari Homma**, Gifu (JP); **Koichi Kawashima**, Kyoto (JP); **Koji Katayama**, Nara (JP); **Shinichi Yoneda**, Kyoto (JP)

(73) Assignee: **NUVOTON TECHNOLOGY CORPORATION JAPAN**, Kyoto (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 694 days.

(21) Appl. No.: **17/459,262**

(22) Filed: **Aug. 27, 2021**

(65) **Prior Publication Data**

US 2021/0389264 A1 Dec. 16, 2021

Related U.S. Application Data

(63) Continuation of application No. PCT/JP2020/000803, filed on Jan. 14, 2020.

(30) **Foreign Application Priority Data**

Mar. 7, 2019 (JP) 2019-042012

(51) **Int. Cl.**
G01N 27/12 (2006.01)
B60K 15/03 (2006.01)
B60L 50/70 (2019.01)

(52) **U.S. Cl.**
CPC ***G01N 27/12*** (2013.01); ***B60K 15/03006*** (2013.01); ***B60L 50/70*** (2019.02); *B60K 2015/03315* (2013.01)

(58) **Field of Classification Search**
CPC G01N 27/12; G01N 27/125; G01N 33/005; B60K 15/03006; B60K 2015/03315;
(Continued)

(56) **References Cited**

U.S. PATENT DOCUMENTS

7,356,420 B2 * 4/2008 Vilanova G01N 33/146 702/22
2007/0054170 A1 * 3/2007 Isenberg H01B 1/122 429/495

(Continued)

FOREIGN PATENT DOCUMENTS

JP S59-058348 A 4/1984
WO 2013/051267 A1 4/2013
WO WO-2017037984 A1 * 3/2017 ..... B60K 15/063

OTHER PUBLICATIONS

International Search Report and Written Opinion issued on Mar. 24, 2020 in International Patent Application No. PCT/JP2020/000803; with partial English translation.

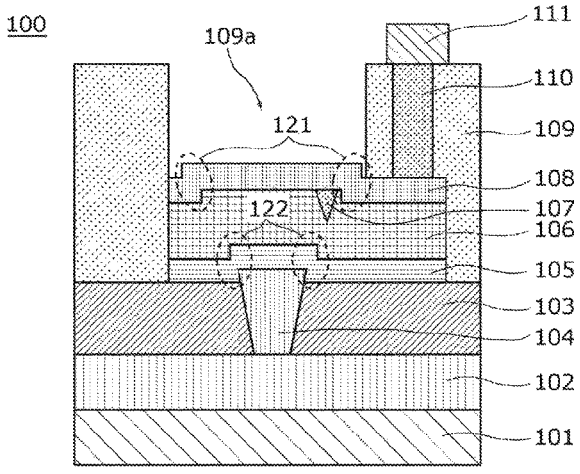
(Continued)

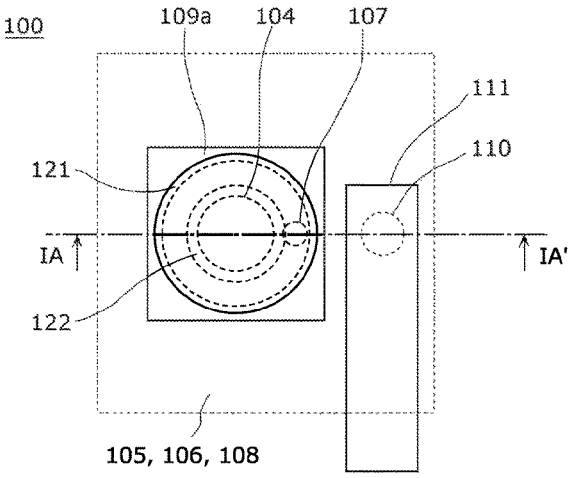
Primary Examiner — Joseph J Dallo
(74) *Attorney, Agent, or Firm* — Rimon P.C.

(57) **ABSTRACT**

A gas sensor includes a gas detecting element that includes a first electrode, a metal oxide layer, and a second electrode; and a first insulating film that has an opening allowing the second electrode to be partially exposed therethrough and covers the first electrode, the metal oxide layer, and another part of the second electrode. The metal oxide layer has a characteristic where its resistance value changes as the second electrode makes contact with gas molecules including hydrogen atoms. A first step is provided at a portion lying on an interface between the metal oxide layer and the second electrode and located within the opening as viewed in plan view. A local region is provided in the metal oxide layer and near the first step. A degree of oxygen deficiency of the local

(Continued)





region is greater than a degree of oxygen deficiency of other regions in the metal oxide layer.

13 Claims, 18 Drawing Sheets

(58) **Field of Classification Search**
CPC .. B60K 1/00; B60K 15/07; B60K 2001/0411; B60K 2015/0638; B60L 50/70; B60L 50/72; B60Y 2400/202; Y02E 60/50; Y02T 90/40; H01M 8/00; H01M 8/04
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2009/0301898	A1*	12/2009	Backhaus-Ricoult	H01M 4/8605 205/724
2013/0202489	A1*	8/2013	Ong	G01N 33/005 977/902
2013/0250658	A1	9/2013	Wei et al.	
2017/0131227	A1*	5/2017	Homma	H01M 8/0444
2017/0241933	A1*	8/2017	Fujii	G01N 33/005
2017/0269043	A1*	9/2017	Homma	G01N 33/005
2017/0307556	A1*	10/2017	Muraoka	G01N 33/0031
2017/0307557	A1*	10/2017	Muraoka	G01N 27/125

OTHER PUBLICATIONS

J.Yu et al., "Hydrogen gas sensing properties of Pt/Ta2O5 Schottky diodes based on Si and SiC substrates," Sensors and Actuators A 172 (2011) pp. 9-14.

Toshiyuki Usagawa et al., "A Novel Pt—Ti—O Gate Si-Metal-Insulator-Semiconductor Field-Effect Transistor Hydrogen Gas Sensor," IEEE Sensors 2010 Conference, pp. 2145-2148.

Ikuo Takahashi, "Catalytic Combustion Type Hydrogen Gas Sensor," Journal of the Surface Finishing Society of Japan, vol. 57, No. 4, 2006, pp. 267-270; with parcial English translation.

Hisao Kitaguchi, "The present situation and some subjects of the hydrogen gas sensor," Hydrogen Energy Systems, vol. 30, No. 2, 2005, pp. 35-40; with English abstract.

* cited by examiner

FIG. 1A

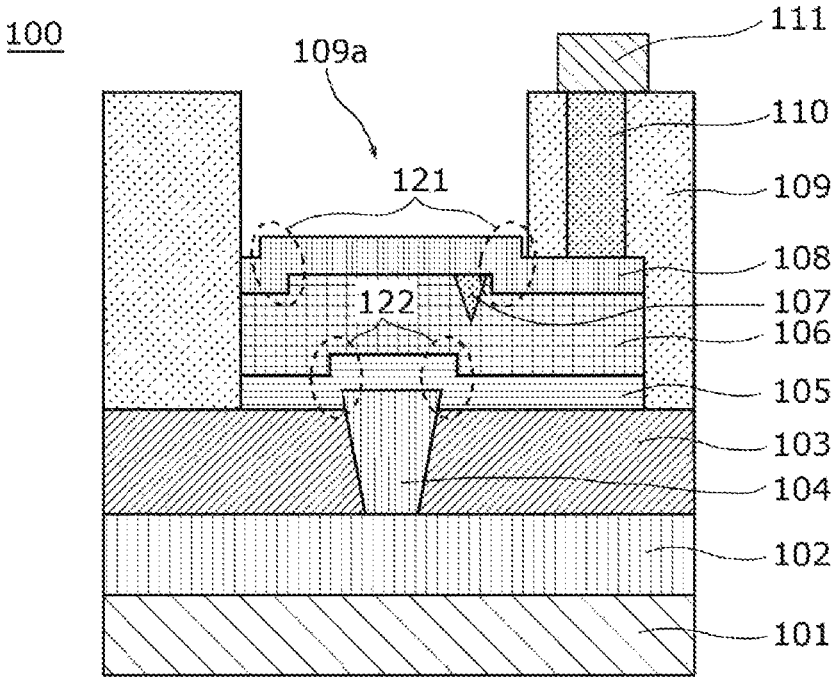

100
109a
111
110
121
109
108
122
107
106
105
103
104
102
101

FIG. 1B

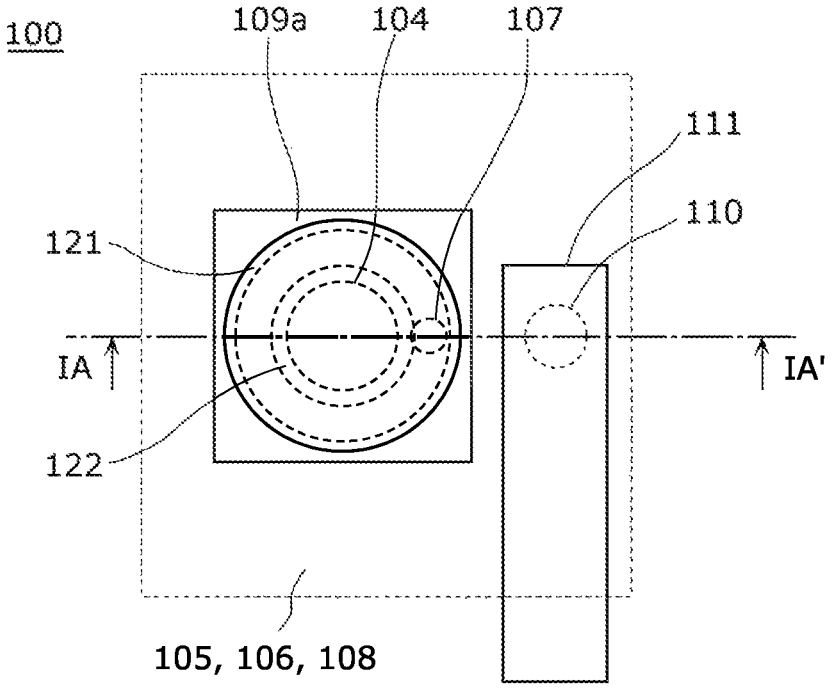

100
109a
104
107
111
110
121
IA
IA'
122
105, 106, 108

FIG. 2A

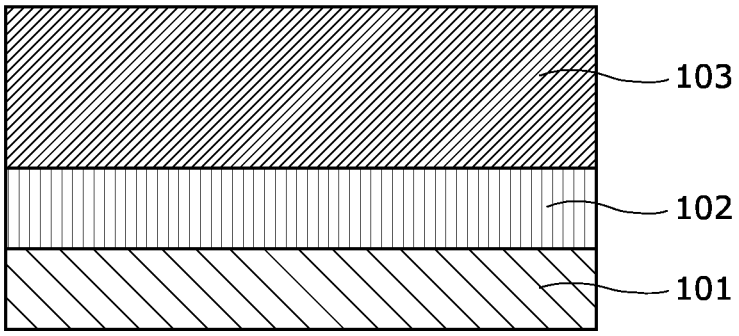


FIG. 2B

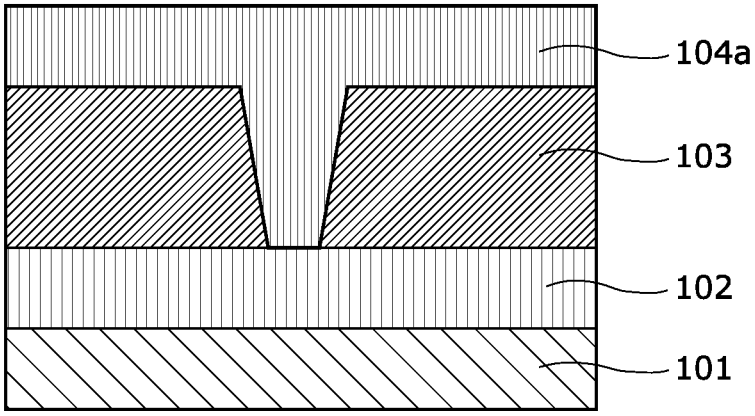


FIG. 2C

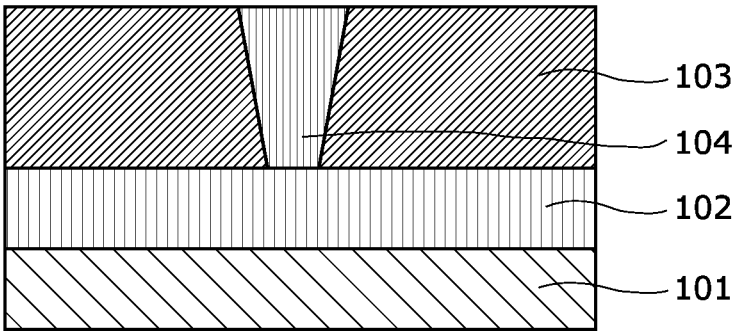


FIG. 2D

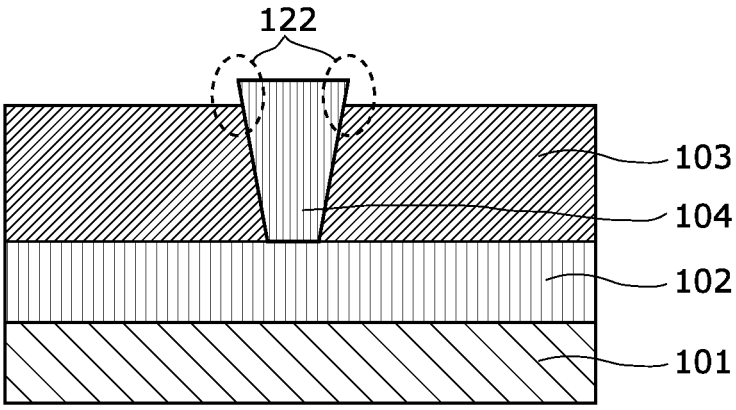


FIG. 2E

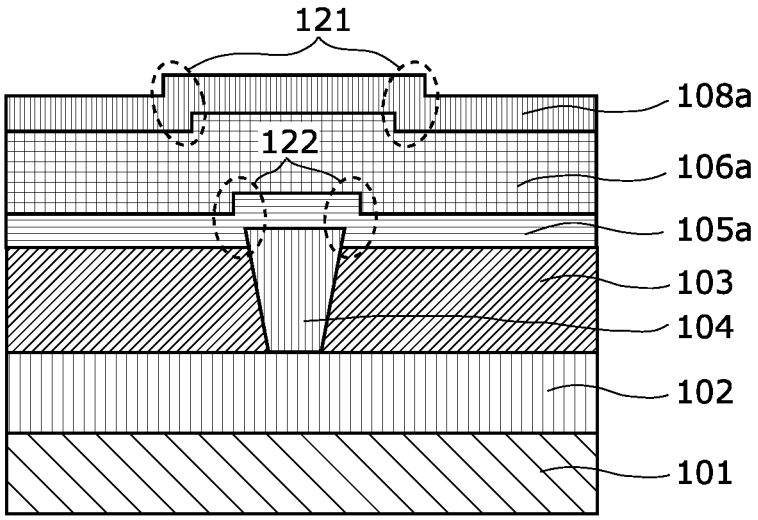

121
122
108a
106a
105a
103
104
102
101

FIG. 2F

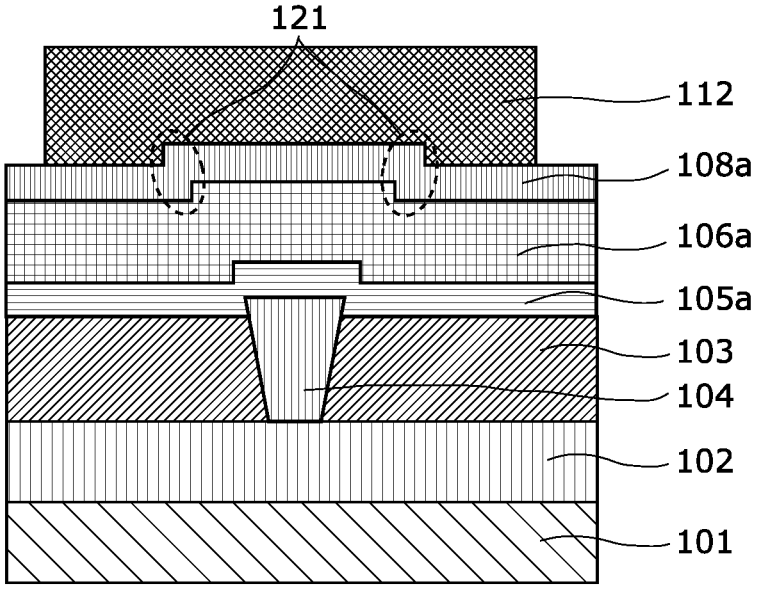

121
112
108a
106a
105a
103
104
102
101

FIG. 2G

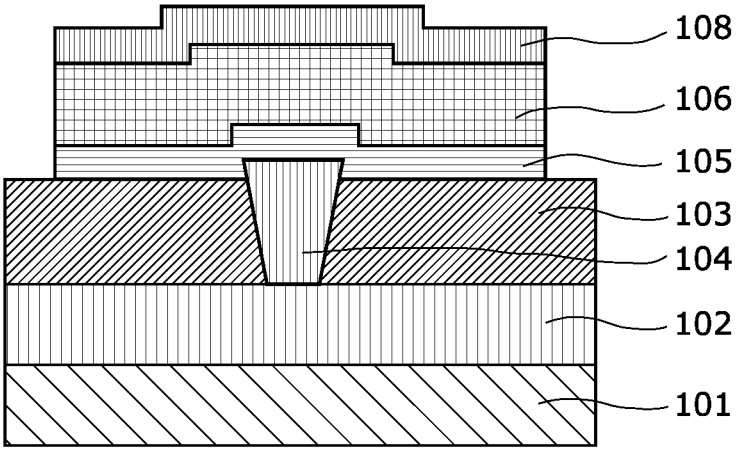

108
106
105
103
104
102
101

FIG. 2H

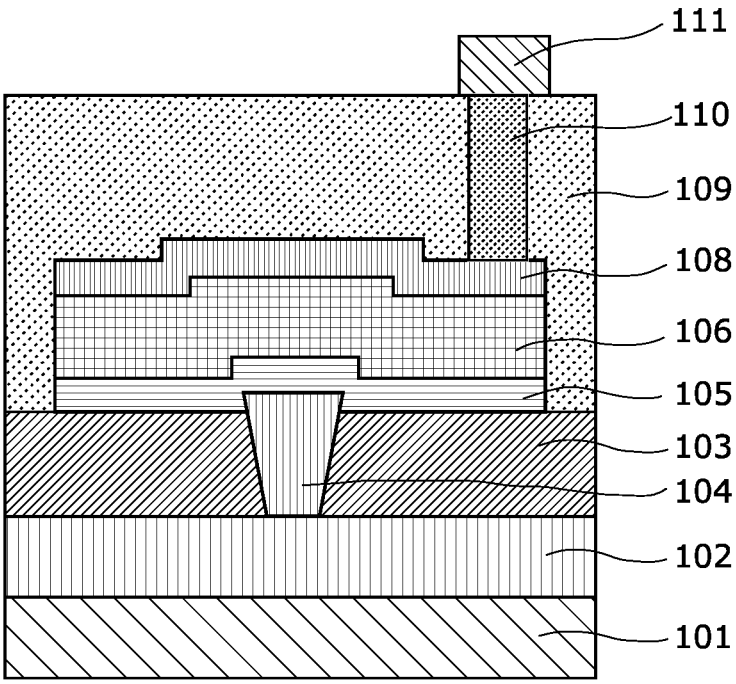

111
110
109
108
106
105
103
104
102
101

FIG. 2I

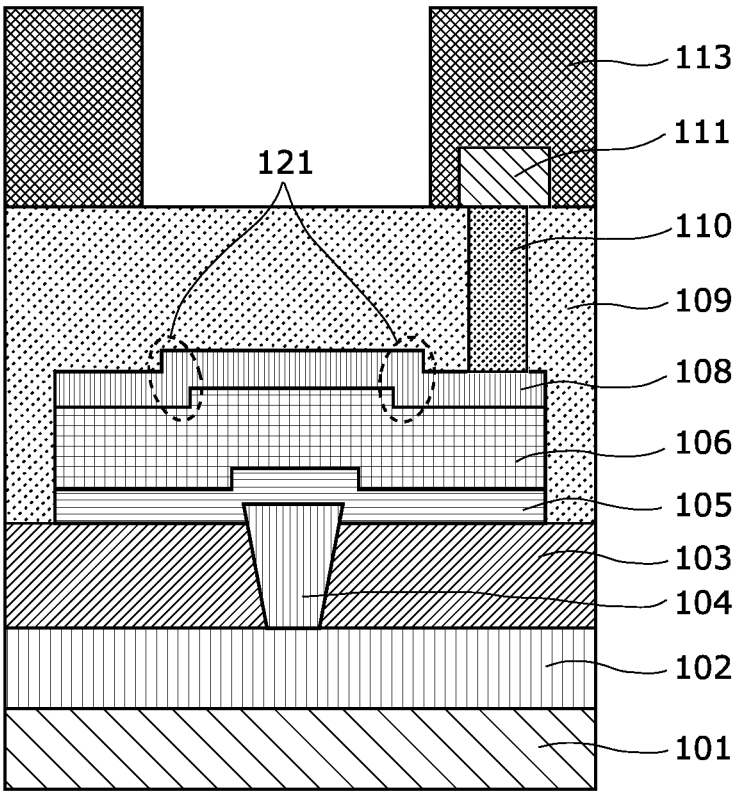


FIG. 2J

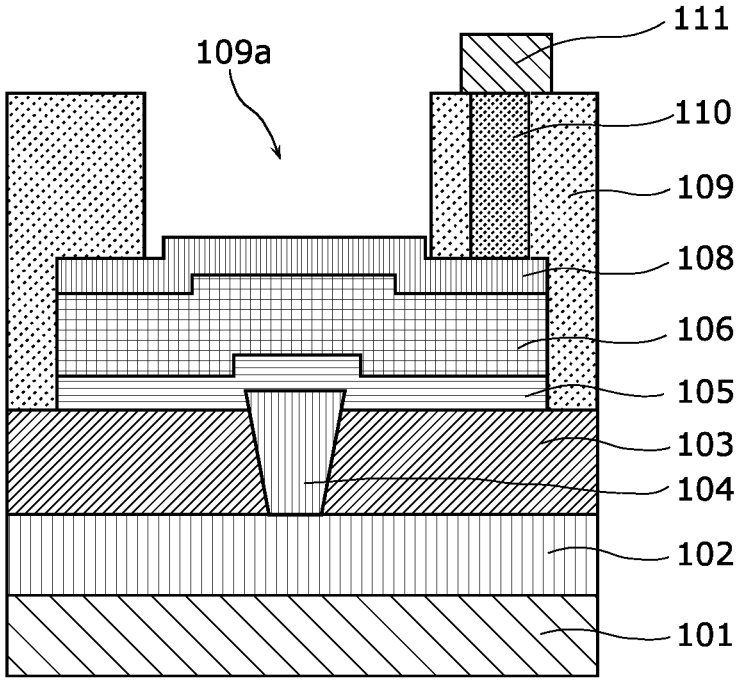

111
109a
110
109
108
106
105
103
104
102
101

FIG. 3

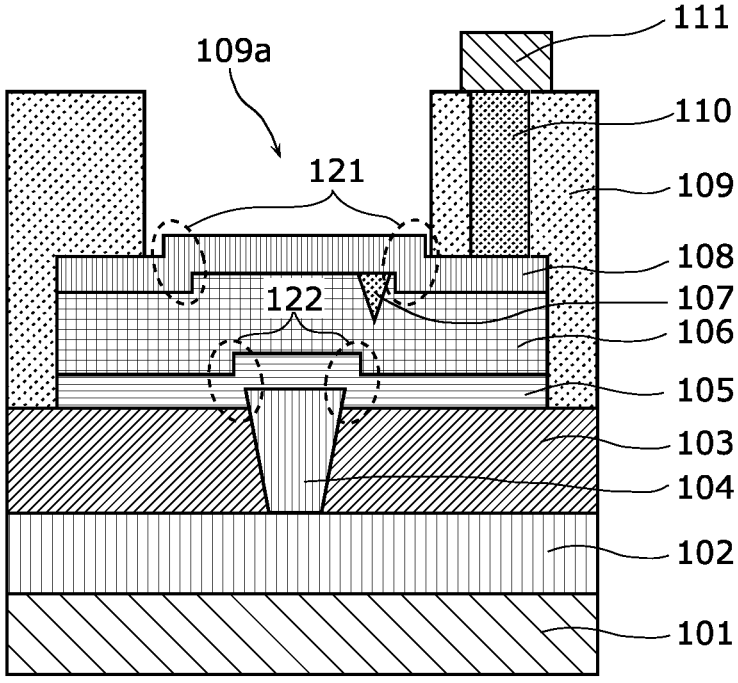

111
109a
110
121
109
108
122
107
106
105
103
104
102
101

FIG. 4

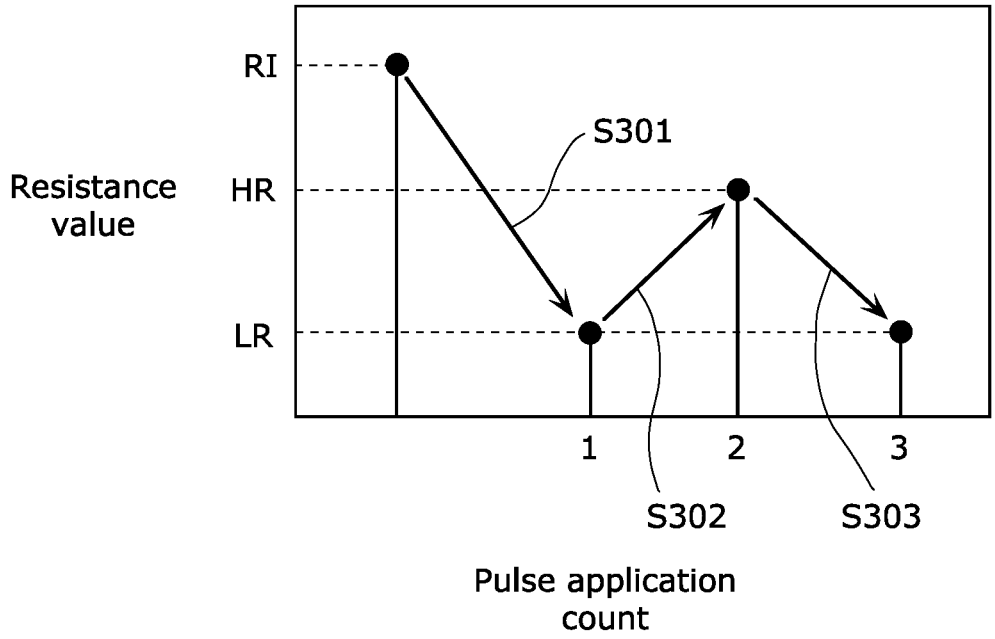

RI
HR
LR
Resistance value
S301
1
2
3
S302
S303
Pulse application count

FIG. 5

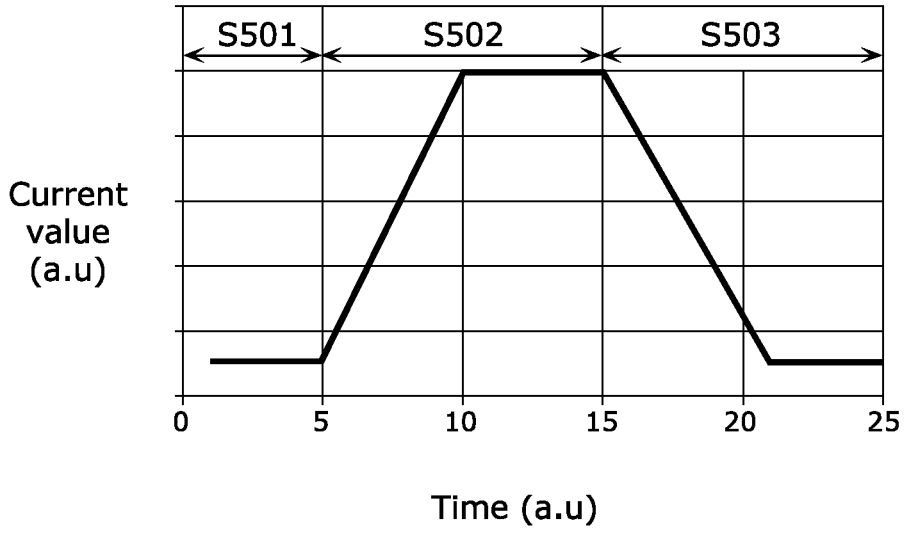

S501
S502
S503
Current value (a.u)
0
5
10
15
20
25
Time (a.u)

FIG. 6

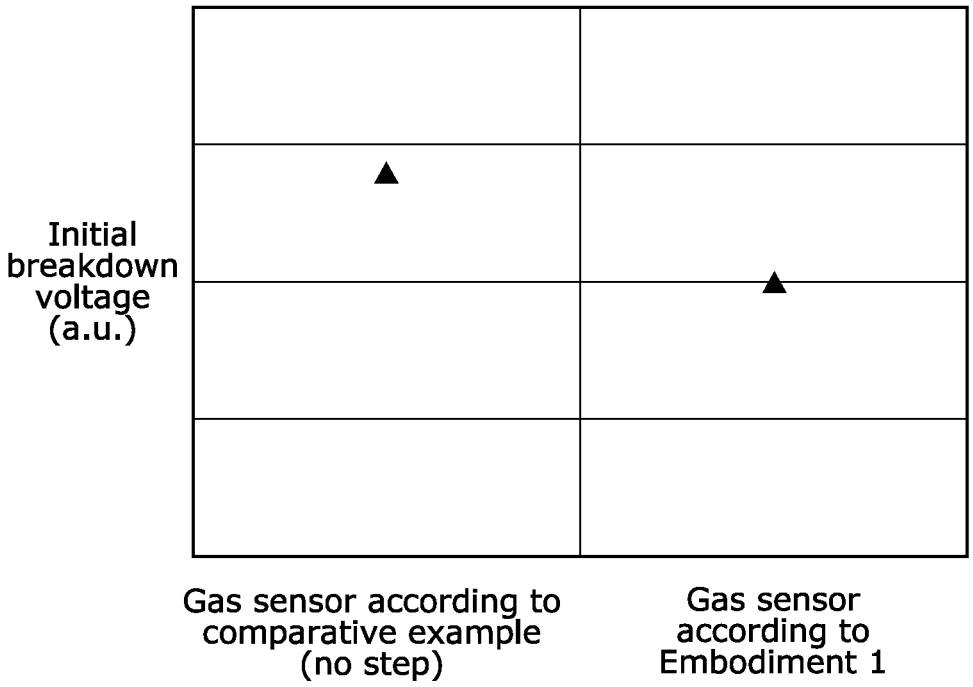

Initial breakdown voltage (a.u.)
Gas sensor according to comparative example (no step)
Gas sensor according to Embodiment 1

FIG. 7

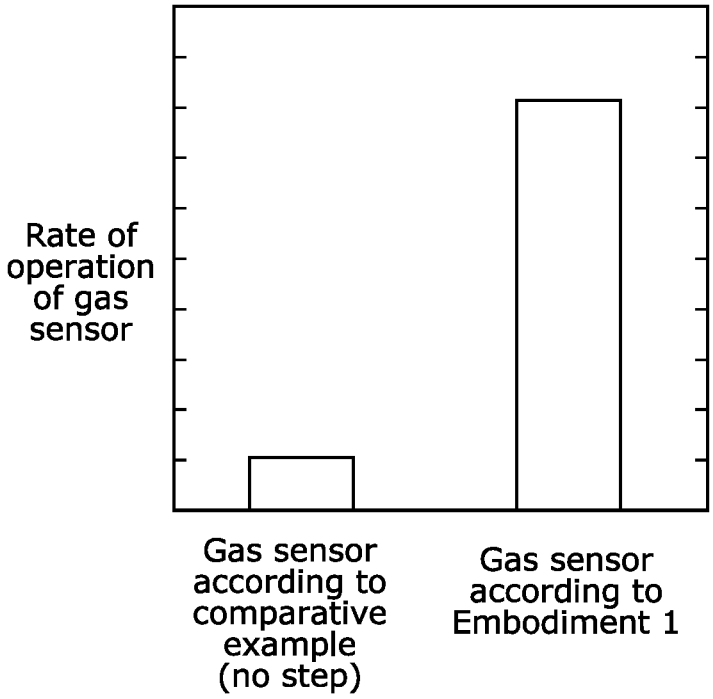

Rate of operation of gas sensor
Gas sensor according to comparative example (no step)
Gas sensor according to Embodiment 1

FIG. 8A

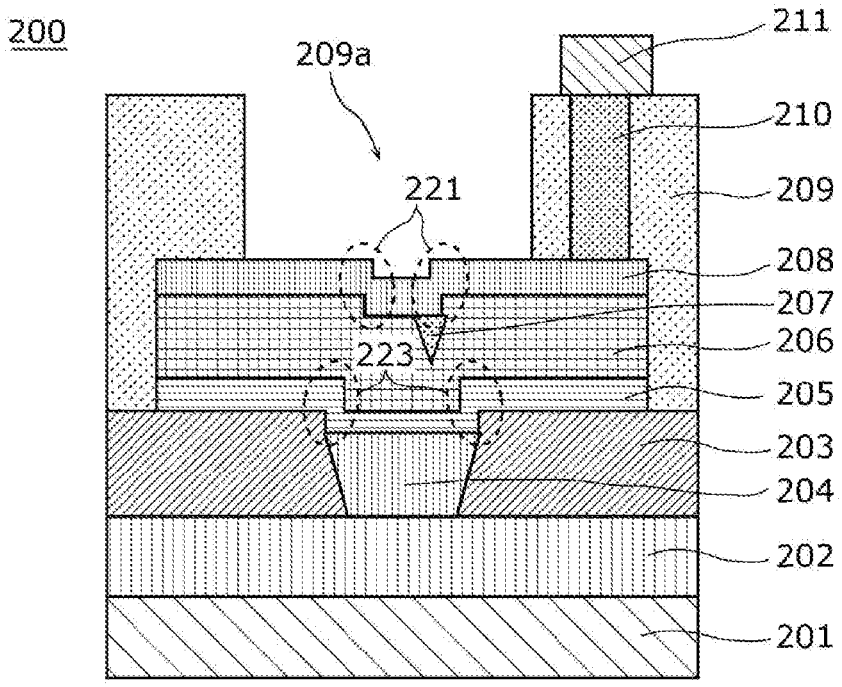

200
209a
211
210
221
209
208
207
206
223
205
203
204
202
201

FIG. 8B

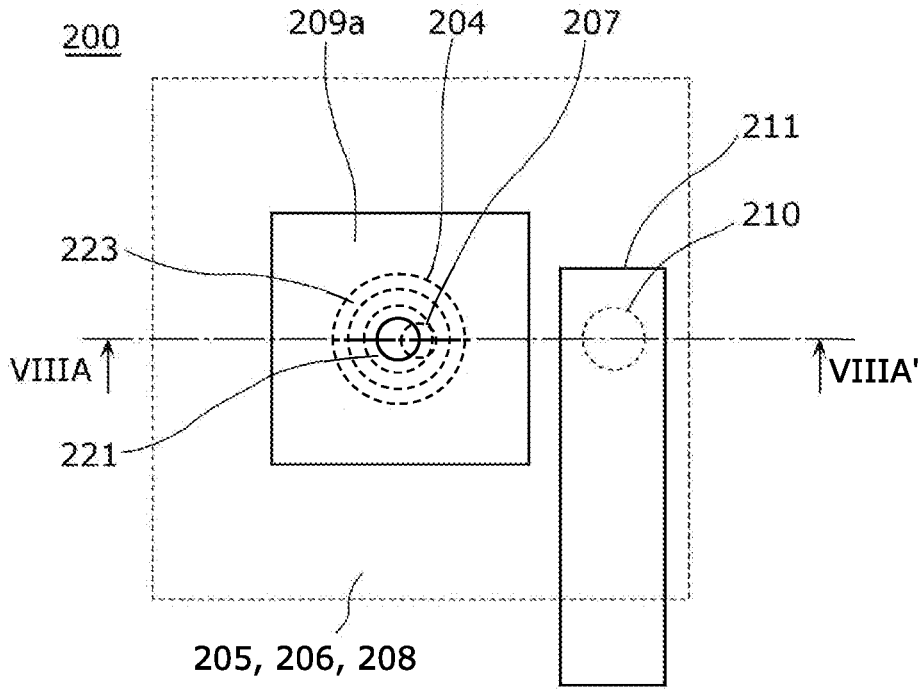

200
209a
204
207
211
210
223
VIIIA
VIIIA'
221
205, 206, 208

FIG. 9A

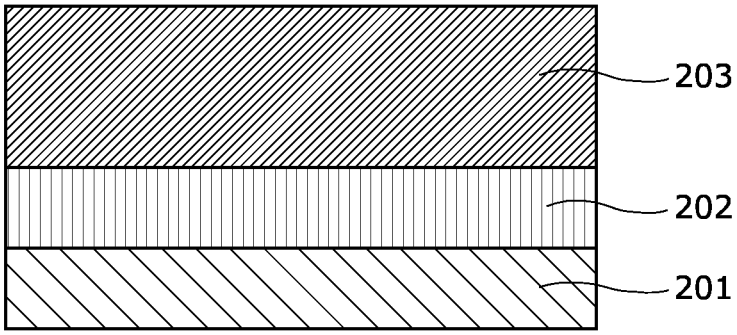


FIG. 9B

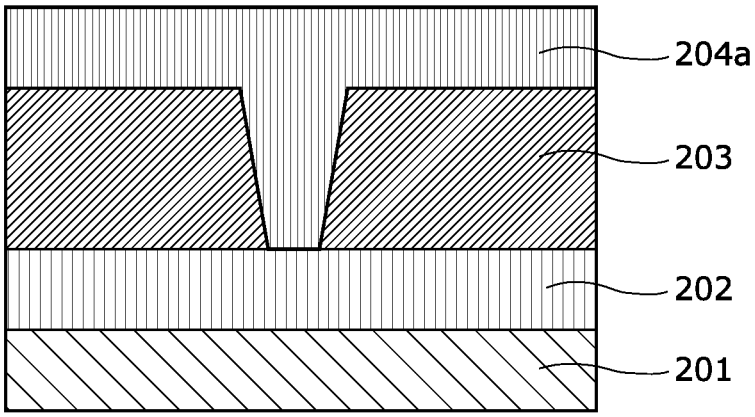


FIG. 9C

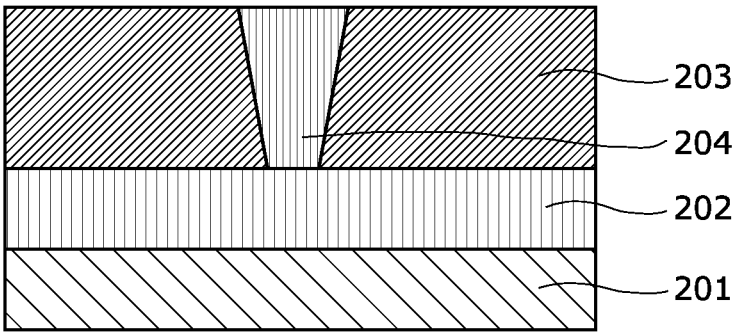


FIG. 9D

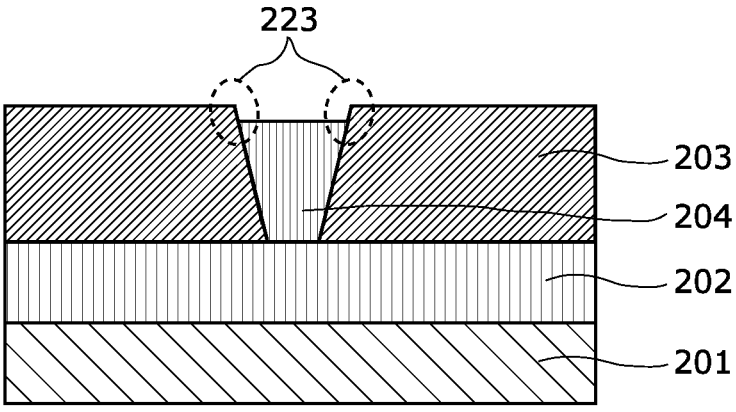


FIG. 9E

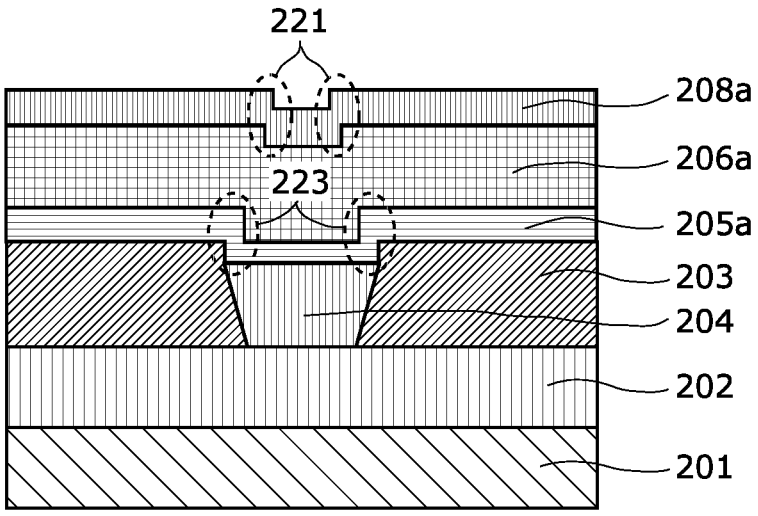

221
208a
206a
223
205a
203
204
202
201

FIG. 9F

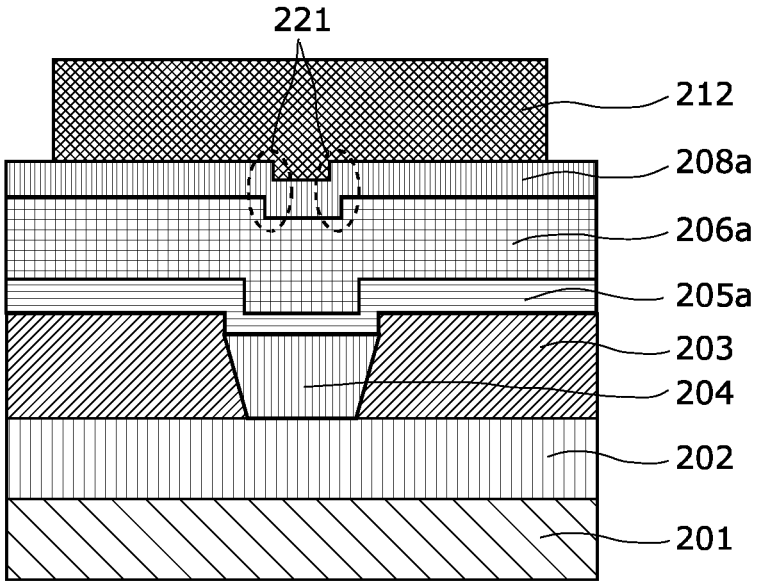

221
212
208a
206a
205a
203
204
202
201

FIG. 9G

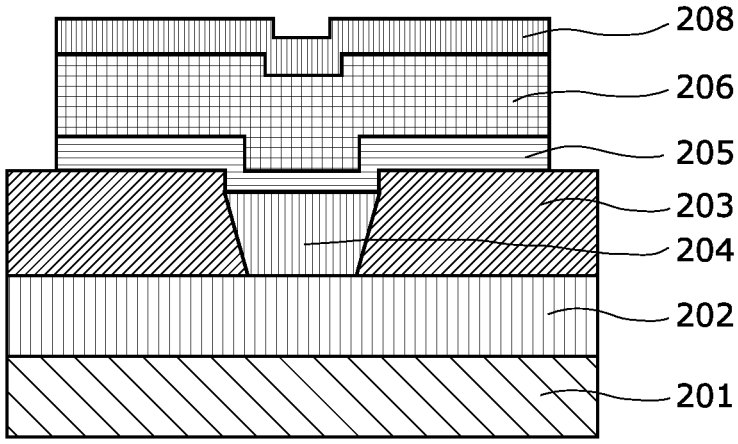

208
206
205
203
204
202
201

FIG. 9H

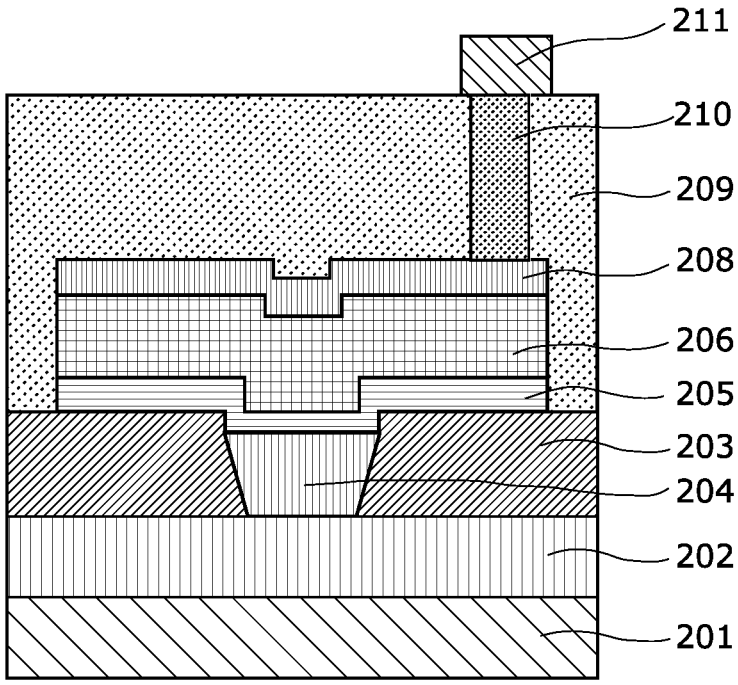

211
210
209
208
206
205
203
204
202
201

FIG. 9I

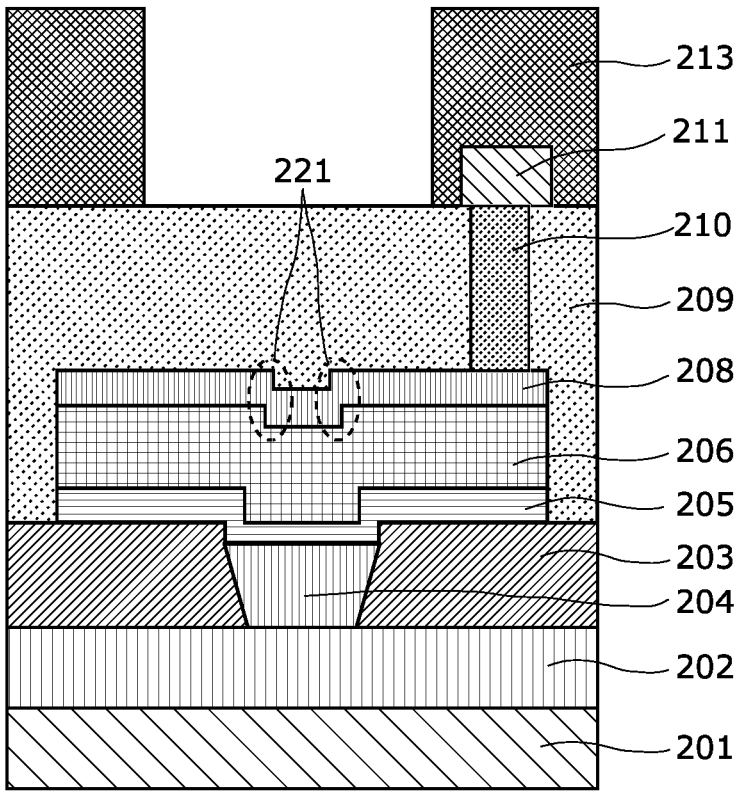


FIG. 9J

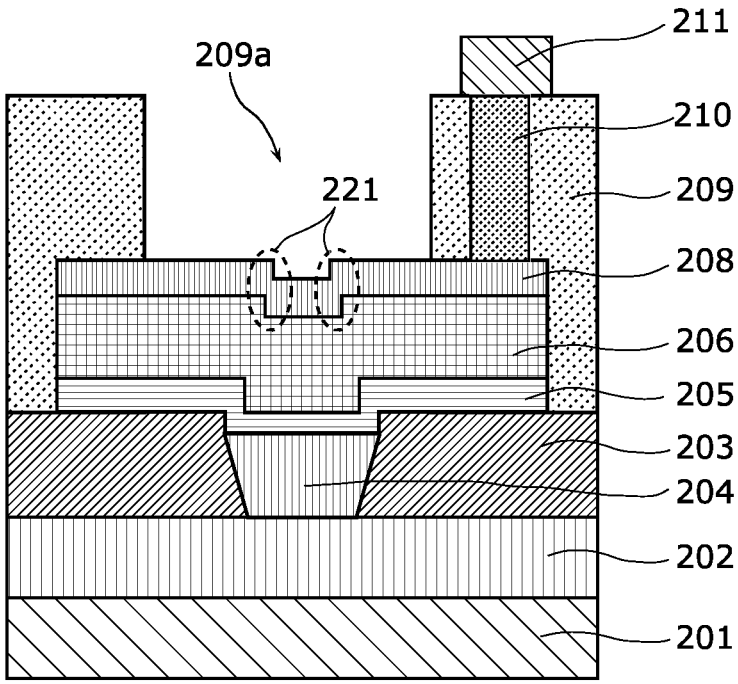


FIG. 10

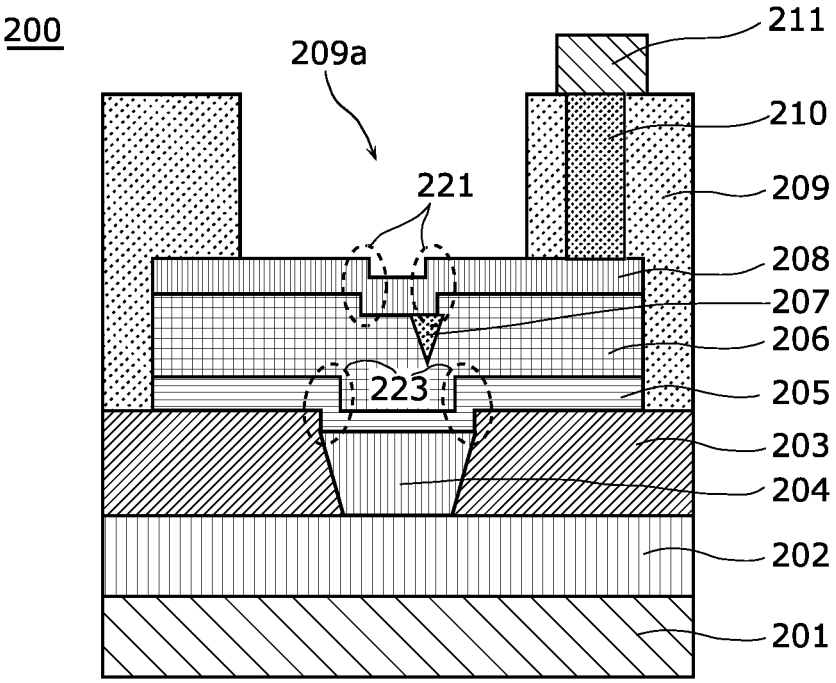
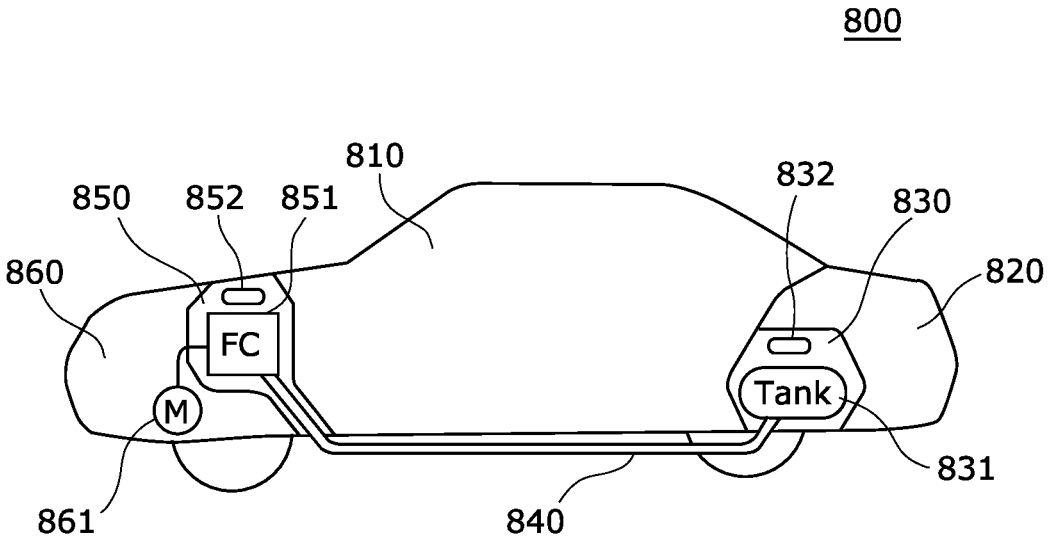


FIG. 11



GAS SENSOR, METHOD OF MANUFACTURING GAS SENSOR, AND FUEL CELL VEHICLE

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation application of PCT International Application No. PCT/JP2020/000803 filed on Jan. 14, 2020, designating the United States of America, which is based on and claims priority of Japanese Patent Application No. 2019-042012 filed on Mar. 7, 2019. The entire disclosures of the above-identified applications, including the specifications, drawings and claims are incorporated herein by reference in their entirety.

FIELD

The present disclosure relates to a gas sensor, a method of manufacturing the gas sensor, and a fuel cell vehicle provided with the gas sensor.

BACKGROUND

Nowadays, vigorous efforts are being made in various fields toward realizing a hydrogen-powered society. In particular, hydrogen-fueled fuel cell vehicles that are expected to be the ultimate environmentally friendly vehicles have been released into the market, and as such, infrastructures such as hydrogen stations are steadily being made available. Such circumstances have led to increased importance of sensors that detect hydrogen to ensure the safety and the comfort in a hydrogen-powered society.

Among sensors that detect a gas represented by hydrogen, there is known a gas sensor that includes a gas detecting element of a metal-insulator-metal (MIM) structure, in which a gas sensitive insulating film (also referred to below simply as an insulating film) and metal films are laminated together.

Such a gas sensor can be used to detect, for example, hydrogen, alcohol, hydrocarbon, ammonia, or amine contained in a trace amount in a gas, and such a gas sensor can detect, in particular, a highly reactive gas, such as hydrogen, with high efficiency.

PTL 1 discloses a gas sensor of the MIM structure, in which an insulating film and metal films are laminated together. In the gas sensor disclosed in PTL 1, an insulating film obtained by adding a predetermined amount of palladium and glass to tantalum pentoxide (Ta_2O_5) is used, and platinum (Pt) is used as an upper and a lower metal electrode that sandwich the insulating film.

CITATION LIST

Patent Literature

PTL 1: Japanese Unexamined Patent Application Publication No. S59-058348

Non Patent Literature

NPL 1: J. Yu et al. "Hydrogen gas sensing properties of Pt/Ta2O5 Schottky Diodes based on Si and SiC substrates." Sensors and Actuators A 172 (2011) pp. 9-14

NPL 2: Toshiyuki Usagawa et al. "A Novel Pt—Ti—O Gate Si-Metal-Insulator-Semiconductor Field-Effect Transistor." IEEE SENSORS 2010 Conference, pp. 2145-2148

NPL 3: Ikuo Takahashi, "Catalytic Combustion Type Hydrogen Gas Sensor," Journal of The Surface Finishing Society of Japan, Vol. 57, No. 4, 2006, pp. 267-270

NPL 4: Hisao Kitaguchi, "The present situation and some subjects of the hydrogen gas sensor," Hydrogen Energy Systems, Vol. 30, No. 2 (2005), pp. 35-40

SUMMARY

Technical Problem

Despite the above, with the existing gas detecting elements, the gas detecting elements are heated to 100° C. or higher in order to improve the sensitivity for detecting a gas containing hydrogen atoms, for example, and the required power consumption of even the smallest gas detecting element is around 100 mW. Accordingly, when such a gas detecting element is kept ON during use, the gas detecting element disadvantageously consumes a very large amount of power.

The present disclosure provides a gas sensor that is less power consuming and is capable of detecting a gas molecule containing a hydrogen atom stably and with high sensitivity. The present disclosure further provides a method of manufacturing such a gas sensor and a fuel cell vehicle.

Solution to Problem

To address the existing problem, a gas sensor according to one aspect of the present disclosure includes: a gas detecting element that includes a first electrode, a metal oxide layer provided on the first electrode, and a second electrode provided on the metal oxide layer, the gas detecting element detecting a gas molecule existing in a gas and including a hydrogen atom; and a first insulating film having an opening that allows a part of the second electrode to be exposed therethrough, the first insulating film covering the first electrode, the metal oxide layer, and another part of the second electrode, wherein the metal oxide layer has a characteristic in which a resistance value of the metal oxide layer changes when the second electrode comes into contact with the gas molecule, a first step is provided at a portion lying on an interface between the metal oxide layer and the second electrode and located within the opening as viewed in plan view, a local region is provided in the metal oxide layer and close to the first step, and a degree of oxygen deficiency of the local region is greater than a degree of oxygen deficiency of a region other than the local region in the metal oxide layer.

A method of manufacturing a gas sensor according to one aspect of the present disclosure includes: forming a first electrode film on a substrate; forming a metal oxide film on the first electrode film, the metal oxide film including an upper surface provided with a first step; forming a second electrode film on the metal oxide film; forming a gas detecting element including a first electrode, a metal oxide layer, and a second electrode by patterning the first electrode film, the metal oxide film, and the second electrode film so as to include the first step as viewed in plan view; forming a first insulating film so as to cover the gas detecting element; and forming an opening by removing a part of the first insulating film, the opening allowing a part of the second electrode on the first step to be exposed therethrough as viewed in plan view.

A fuel cell vehicle according to one aspect of the present disclosure includes: a passenger compartment; a gas tank compartment housing a hydrogen gas tank; a fuel cell

compartment housing a fuel cell; and the gas sensor according to claim **1**, wherein the gas sensor is provided in at least one of the gas tank compartment or the fuel cell compartment.

Advantageous Effects

The present disclosure can provide a gas sensor that is less power consuming and is capable of detecting a gas molecule containing a hydrogen atom stably and with high sensitivity. The present disclosure can further provide a method of manufacturing such a gas sensor and a fuel cell vehicle.

BRIEF DESCRIPTION OF DRAWINGS

These and other advantages and features will become apparent from the following description thereof taken in conjunction with the accompanying Drawings, by way of non-limiting examples of embodiments disclosed herein.

FIG. **1**A is a cross-sectional view of a gas sensor according to Embodiment 1.

FIG. **1**B is a plan view of the gas sensor according to Embodiment 1.

FIG. **2**A is a cross-sectional view illustrating a method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**B is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**C is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**D is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**E is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**F is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**G is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**H is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**I is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **2**J is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 1.

FIG. **3** is a cross-sectional view of the gas sensor according to Embodiment 1.

FIG. **4** illustrates a method of forming a local region in the gas sensor according to Embodiment 1.

FIG. **5** is a graph illustrating a result of evaluating the gas sensor according to Embodiment 1.

FIG. **6** illustrates a result of evaluating a no-step gas sensor and the gas sensor according to Embodiment 1.

FIG. **7** illustrates another result of evaluating the no-step gas sensor and the gas sensor according to Embodiment 1.

FIG. **8**A is a cross-sectional view of a gas sensor according to Embodiment 2.

FIG. **8**B is a plan view of the gas sensor according to Embodiment 2.

FIG. **9**A is a cross-sectional view illustrating a method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**B is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**C is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**D is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**E is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**F is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**G is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**H is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**I is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **9**J is another cross-sectional view illustrating the method of manufacturing the gas sensor according to Embodiment 2.

FIG. **10** is a cross-sectional view of the gas sensor according to Embodiment 2.

FIG. **11** is a side view of a fuel cell vehicle according to Embodiment 3.

DESCRIPTION OF EMBODIMENTS

(Underlying Knowledge Forming Basis of the Present Disclosure)

The present inventors have conducted diligent studies and thus found the following problems with existing gas sensors.

PTL 1 indicates that the disclosed gas sensor can detect an inflammable gas containing hydrogen but does not teach any detailed mechanism for such detection. Thus, with an assumption that a phenomenon similar to the mechanism disclosed in NPL 1 that concerns a gas sensor (Pt—Ta_2O_5—Si) of a metal-insulator-semiconductor (MIS) structure is also induced in the gas sensor disclosed in PTL 1, this mechanism can be described as follows.

First, when a gas containing a hydrogen gas, for example, has come into contact with a surface of platinum, which is a metal having a catalytic effect, the catalytic effect of the platinum causes the hydrogen gas to break down into hydrogen atoms, and these hydrogen atoms take oxygen atoms from the tantalum pentoxide in the insulating film in accordance with the chemical reaction formula shown below. Thus, an oxygen vacancy is formed in the tantalum pentoxide, and this conceivably allows a current to flow more easily.

$$Ta_2O_5+2_XH \rightarrow {}_XH_2O+Ta_2O_{5-X}$$

Meanwhile, when the gas containing the hydrogen gas ceases to exist on the surface of the platinum, the reverse process occurs in accordance with the chemical reaction formula shown below. Thus, the oxygen vacancy in the tantalum pentoxide ceases to exit, which conceivably makes the current flow less easily.

$${}_XH_2O+Ta_2O_{5-X} \rightarrow Ta_2O_5+2_XH$$

Based on such a mechanism, it is conceivable that the MIM structure in which an insulating film obtained by adding a predetermined amount of palladium and glass to tantalum pentoxide is used and platinum is used as an upper and a lower metal electrode that sandwich the insulating film functions as a gas sensor that detects a gas containing hydrogen atoms.

Moreover, in the gas sensor of the MIM structure described in PTL 1, a heater is provided adjacent to the gas detecting element. At the time of carrying out a measurement, a predetermined voltage is applied to the heater, and thus the temperature of the gas detecting element is raised to 400° C. This is conceivably for raising the detection sensitivity of the gas detecting element. In other words, although the hydrogen gas is dissociated into hydrogen atoms by use of platinum, which is a metal having a catalytic effect, since the rate of dissociating molecules containing hydrogen atoms into the hydrogen atoms through the catalytic effect is proportional to the rise in the temperature, it is considered that the detection sensitivity increases in accordance with the rise in the temperature of the gas detecting element.

Not only in the gas sensor of the MIM structure but also in a gas sensor of the MIS structure that utilizes the catalytic effect of a metal, a heater is provided adjacent to a gas detecting element, and the gas sensor is used normally with its surrounding temperature retained at 100° C. or higher. For example, in the gas sensor in which the MIS structure is used as a diode as disclosed in NPL 1 described above, the temperature of 100° C. or higher is required to carry out a detection. Moreover, the gas sensor in which the MIS structure is used as a transistor as disclosed in NPL 2 is made to operate with its surrounding temperature held at 115° C.

Furthermore, the contact combustion gas sensor disclosed in NPL 3 is also one of the gas sensors in which the catalytic effect of a metal is used, and in this contact combustion gas sensor as well, the gas detecting element is heated to 200° C. to 300° C. in operation.

Meanwhile, the hot wire semiconductor gas sensor and the thermal conduction gas sensor disclosed in NPL 4 are gas sensors in which the catalytic effect of a metal is not used, but even in these gas sensors, the gas detecting element is heated to 100° C. or higher.

In this manner, with the existing gas detecting elements, the gas detecting elements are heated to 100° C. or higher in order to improve the sensitivity for detecting a gas containing hydrogen atoms, and even the smallest gas detecting element consumes around 100 mW of power. Accordingly, when these gas detecting elements are kept ON during use, the gas detecting elements disadvantageously consume a very large amount of power.

A gas sensor according to one aspect of the present disclosure is capable of detecting a gas molecule containing a hydrogen atom stably and with high sensitivity and also excels in the power saving performance.

(Aspects of the Present Disclosure)

A gas sensor, a method of manufacturing a gas sensor, and a fuel cell vehicle according to some aspects of the present disclosure include features such as those described below.

A gas sensor according to one aspect of the present disclosure includes a gas detecting element and a first insulating film. The gas detecting element includes a first electrode, a metal oxide layer provided on the first electrode, and a second electrode provided on the metal oxide layer. The gas detecting element detects a gas molecule existing in a gas and including a hydrogen atom. The first insulating film has an opening that allows a part of the second electrode to be exposed therethrough. The first insulating film covers the first electrode, the metal oxide layer, and another part of the second electrode. The metal oxide layer has a characteristic in which a resistance value of the metal oxide layer changes as the second electrode comes into contact with the gas molecule. A first step is provided at a portion lying on an interface between the metal oxide layer and the second electrode and located within the opening as viewed in plan view. A local region is provided in the metal oxide layer and near the first step. A degree of oxygen deficiency of the local region is greater than a degree of oxygen deficiency of a region other than the local region in the metal oxide layer.

In the gas sensor according to one aspect of the present disclosure, the first step may have an upwardly convex shape.

The gas sensor according to one aspect of the present disclosure may further include a first contact plug provided between a substrate and the first electrode. The first contact plug may include a side surface surrounding the first contact plug, and the side surface may be covered by a second insulating film. The first contact plug may have an upper surface that projects from an upper surface of the second insulating film. The first electrode may include a second step provided across the upper surface of the first contact plug and the upper surface of the second insulating film surrounding the first contact plug. The first step may be a step resulting from a transfer of the second step onto an upper surface of the metal oxide layer.

In the gas sensor according to one aspect of the present disclosure, the first step may have a downwardly convex shape.

The gas sensor according to one aspect of the present disclosure may further include a first contact plug provided between a substrate and the first electrode. A side surface surrounding the first contact plug may be covered by a second insulating film. An upper surface of the first contact plug may be recessed from an upper surface of the second insulating film. The first electrode may include a third step provided across the upper surface of the first contact plug and the upper surface of the second insulating film surrounding the first contact plug. The first step may be a step resulting from a transfer of the third step onto an upper surface of the metal oxide layer.

In the gas sensor according to one aspect of the present disclosure, the second electrode may include a material having a catalytic effect of dissociating the gas molecule into the hydrogen atom.

In the gas sensor according to one aspect of the present disclosure, the second electrode may include platinum or palladium.

In the gas sensor according to one aspect of the present disclosure, the metal oxide layer may transition reversibly between a high-resistance state and a low-resistance state in accordance with a voltage applied across the first electrode and the second electrode.

The gas sensor according to one aspect of the present disclosure may further include a current detector that detects a current that flows in the metal oxide layer when a predetermined voltage is applied across the first electrode and the second electrode. A decrease in the resistance value may be detected based on an increase in the current detected by the current detector.

In the gas sensor according to one aspect of the present disclosure, the metal oxide layer may include a transition metal oxide.

In the gas sensor according to one aspect of the present disclosure, the transition metal oxide may be any one of tantalum oxide, hafnium oxide, or zirconium oxide.

The gas sensor according to one aspect of the present disclosure may further include a second contact plug penetrating through a part of a portion of the first insulating film where the first insulating film covers the second electrode and connected to the second electrode, and a conductor connected to the second contact plug at an upper side of the second contact plug.

A method of manufacturing a gas sensor according to one aspect of the present disclosure includes: forming a first electrode film on a substrate; forming a metal oxide film on the first electrode film, the metal oxide film including an upper surface provided with a first step; forming a second electrode film on the metal oxide film; forming a gas detecting element including a first electrode, a metal oxide layer, and a second electrode by patterning the first electrode film, the metal oxide film, and the second electrode film so as to include the first step as viewed in plan view; forming a first insulating film so as to cover the gas detecting element; and forming an opening by removing a part of the first insulating film, the opening allowing a part of the second electrode on the first step to be exposed therethrough as viewed in plan view.

The method of manufacturing a gas sensor according to one aspect of the present disclosure may further include: forming a second insulating film on the substrate; forming a first contact plug in the second insulating film; and removing an upper portion of the second insulating film surrounding the first contact plug so that an upper surface of the first contact plug projects from an upper surface of the second insulating film surrounding the first contact plug by. The first electrode film, the metal oxide film, and the second electrode film may be formed in this order on the first contact plug and the second insulating film so as to cross over a second step, and the gas detecting element including the first step resulting from a transfer of the second step may be formed. The second step may be a step between the upper surface of the first contact plug and the upper surface of the second insulating film surrounding the first contact plug.

The method of manufacturing a gas sensor according to one aspect of the present disclosure may further include: forming a second insulating film on the substrate; forming a first contact plug in the second insulating film; and removing an upper portion of the first contact plug so that an upper surface of the first contact plug is recessed from an upper surface of the second insulating film surrounding the first contact plug. The first electrode film, the metal oxide film, and the second electrode film may be formed in this order on the first contact plug and the second insulating film so as to cross over a third step, and the gas detecting element including the first step resulting from a transfer of the third step may be formed. The third step may be a step between the upper surface of the first contact plug and the upper surface of the second insulating film surrounding the first contact plug.

A fuel cell vehicle according to one aspect of the present disclosure includes a passenger compartment, a gas tank compartment housing a hydrogen gas tank, a fuel cell compartment housing a fuel cell, and the gas sensor according to any one of the above aspects. The gas sensor is provided in at least one of the gas tank compartment or the fuel cell compartment.

Hereinafter, some embodiments of the present disclosure will be described with reference to the drawings.

In the drawings, substantially identical configurations and operations and elements representing substantially identical effects are given identical reference characters, and duplicate descriptions thereof will be omitted. In addition, the numerical values, the materials, the deposition methods, and so on described below are all illustrative in nature and are merely for describing the embodiments of the present disclosure in concrete terms, and the present disclosure is not limited thereby. Moreover, the manners how the constituent elements are connected relative to each other in the following description are illustrative in nature and merely for describing the embodiments of the present disclosure in concrete terms, and how the constituent elements are connected relative to each other to implement the functions of the present disclosure is not limited thereto.

Embodiment 1

Configuration of Gas Sensor

A gas sensor according to Embodiment 1 is a gas sensor of a metal-insulator-metal (MIM) structure in which a metal oxide layer serving as an insulating film and metal films are laminated together. This gas sensor can detect, without being heated by a heater, a hydrogen-containing gas by utilizing the self-heat generation and the gas sensitivity in a local region formed within the metal oxide layer. In this example, the term "hydrogen-containing gas" is a collective term for gasses that include molecules containing hydrogen atoms, and examples of such hydrogen-containing gases can include hydrogen, methane, and alcohol.

FIG. **1**A is a cross-sectional view illustrating an example of a configuration of gas sensor **100** according to the present embodiment.

FIG. **1**B is a top view illustrating an example of the configuration of gas sensor **100** according to the present embodiment.

The cross section illustrated in FIG. **1**A corresponds to the cross section cut along the IA-IA' line indicated in FIG. **1**B and viewed in the direction indicated by the arrows.

Gas sensor **100** includes substrate **101**; first wiring **102**; second insulating film **103** disposed on first wiring **102**; first contact plug **104** penetrating through second insulating film **103** and connected to first wiring **102**; first electrode **105**, metal oxide layer **106**, and second electrode **108** formed in this order from a lower side on second insulating film **103** so as to cover first contact plug **104**; first insulating film **109** that covers at least a part of first electrode **105**, a part of metal oxide layer **106**, and a part of second electrode **108**; second contact plug **110** penetrating through first insulating film **109** and connected to second electrode **108**; and second wiring **111** formed on first insulating film **109** so as to connect to second contact plug **110**.

In this example, an upper surface of first contact plug **104** lies higher than an upper surface of second insulating film **103**, and second step **122** is formed by first contact plug **104** and second insulating film **103** adjacent to first contact plug **104**.

As such, first step **121** is formed in first electrode **105**, metal oxide layer **106**, and second electrode **108** over first contact plug **104**, as second step **122** formed by first contact plug **104** and second insulating film **103** adjacent to first contact plug **104** is transferred to first electrode **105**, metal oxide layer **106**, and second electrode **108**.

Moreover, opening **109***a* is formed in first insulating film **109** over second electrode **108**, and an upper surface of second electrode **108** is exposed through opening **109***a*.

In this example, as illustrated in FIG. **1**B, first step **121** on second electrode **108** is exposed at the bottom of opening **109***a*, and first step **121** is formed as second step **122** formed by first contact plug **104** and second insulating film **103** adjacent to first contact plug **104** is transferred onto second

electrode **108**. First step **121** is of an upwardly convex shape. In this example, it is not essential that first step **121** be exposed on the upper surface of second electrode **108**. It suffices that first step **121** be formed at a portion located within opening **109***a*, as viewed in plan view, at an interface between metal oxide layer **106** and second electrode **108**.

Metal oxide layer **106** is a layer whose resistance value changes reversibly in accordance with an electrical signal given across first electrode **105** and second electrode **108**. For example, metal oxide layer **106** transitions reversibly between a high-resistance state and a low-resistance state in accordance with the voltage applied across first electrode **105** and second electrode **108** and the presence or absence of a hydrogen-containing gas in a gas that comes into contact with second electrode **108**.

Local region **107** is present inside metal oxide layer **106**, and local region **107** is in contact with second electrode **108** but is not in contact with first electrode **105**.

In this example, local region **107** is a small region that includes a filament formed of an oxygen vacant site, and the filament functions as an electrically conductive path.

To be more specific, metal oxide layer **106** is formed of a metal oxide, and the degree of oxygen deficiency of the metal oxide included in local region **107** of metal oxide layer **106** is greater than the degree of oxygen deficiency of the metal oxide included in a portion of metal oxide layer **106** other than local region **107**.

The degree of oxygen deficiency of the metal oxide included in local region **107** changes reversibly in accordance with the voltage applied across first electrode **105** and second electrode **108** and the presence or absence of a hydrogen-containing gas in a gas that comes into contact with second electrode **108** via opening **109***a*.

The "degree of oxygen deficiency" as used in the present specification refers to, with regard to a metal oxide, the proportion of oxygen that is in deficit relative to the amount of oxygen to be contained in the oxide of a stoichiometric composition. When there are a plurality of stoichiometric compositions as the stoichiometric composition of a given metal oxide, the stoichiometric composition of a metal oxide in the present specification means a stoichiometric composition having the highest resistance value among the plurality of stoichiometric compositions.

A metal oxide of the stoichiometric composition is more stable and has a higher resistance value than metal oxides of other composition states outside the stoichiometric composition state.

For example, when a metal is tantalum (Ta), its oxide of the stoichiometric composition of the above definition is Ta_2O_5. Ta_2O_5 can also be expressed as $TaO_{2.5}$. The degree of oxygen deficiency of $TaO_{2.5}$ is 0%.

In one example, the degree of oxygen deficiency of $TaO_{1.5}$ is (2.5−1.5)/2.5=40%. In addition, the degree of oxygen deficiency of an oxygen-excess metal oxide takes a negative value. In the present specification, the degree of oxygen deficiency takes a positive value, 0, or a negative value, unless specifically indicated otherwise.

As such, a metal oxide with a low degree of oxygen deficiency is closer to a metal oxide of the stoichiometric composition and thus has a high resistance value, whereas a metal oxide with a high degree of oxygen deficiency is closer to the metal that is the constituent element of the metal oxide and thus has a low resistance value.

The term "oxygen content by percentage" means the proportion of oxygen atoms with respect to the total number of atoms. For example, the oxygen content by percentage of Ta_2O_5 is the proportion of the oxygen atoms with respect to the total number of atoms (O/(Ta+O)), which is 71.4 atm %. Accordingly, the oxygen content by percentage of a tantalum oxide of an oxygen deficit type is greater than 0 and smaller than 71.4 atm %.

Herein, local region **107** is formed in metal oxide layer **106** as an initial breakdown voltage is applied across first electrode **105** and second electrode **108**. The initial breakdown voltage may be a voltage having a higher absolute value than a normal write voltage applied across first electrode **105** and second electrode **108** so as to cause metal oxide layer **106** to transition reversibly between the high-resistance state and the low-resistance state or may be a voltage having a smaller absolute value than such a write voltage. Moreover, the initial breakdown voltage may be applied repeatedly or applied continuously for a predetermined time.

As the initial breakdown voltage is applied, local region **107** that is in contact with second electrode **108** but is not in contact with first electrode **105** is formed within metal oxide layer **106**, as illustrated in FIG. **1**A.

In this example, local region **107** is produced so as to be concentrated in a portion near first step **121** on metal oxide layer **106**, where first step **121** is formed as second step **122** formed between first contact plug **104** and second insulating film **103** is transferred onto metal oxide layer **106**.

This is because when the initial breakdown voltage is applied across first electrode **105** and second electrode **108**, the electric field is enhanced near first step **121** on metal oxide layer **106** and thus local region **107** is formed more easily particularly in the region near first step **121**.

It is conceivable that local region **107** includes a filament formed of an oxygen vacant site. Moreover, the size of local region **107** is small so as to be in balance with the filament required to pass the current therethrough. Formation of the filament in local region **107** is described by use of a percolation model.

A percolation model is a model that is based on a theory stating that, with the assumption that oxygen vacant sites (simply referred to below as vacant sites) are distributed randomly within local region **107**, the probability that a link between the vacant sites is formed increases when the density of the vacant sites has exceeded a threshold.

According to the percolation model, the filament is formed as a plurality of vacant sites within local region **107** are linked together. Moreover, according to the percolation model, the change in the resistance in metal oxide layer **106** appears due to an occurrence and a disappearance of a vacant site in local region **107**.

In this example, the term "vacant" or "vacancy" means that a metal oxide lacks oxygen from its stoichiometric composition. The expression "the density of vacant sites" corresponds to the degree of oxygen deficiency. In other words, as the degree of oxygen deficiency increases, so does the density of vacant sites.

Local region **107** may be formed only at one location in metal oxide layer **106** of gas sensor **100**. The number of local regions **107** in metal oxide layer **106** can be checked through, for example, an electron beam absorbed current (EBAC) analysis.

As local region **107** is formed in metal oxide layer **106**, the current in metal oxide layer **106** flows concentratedly to local region **107** when the voltage is applied across first electrode **105** and second electrode **108**. Since local region **107** is small, the temperature rises considerably through heat generated by the current of several tens of μA (i.e., power

consumption of less than 0.1 mW) caused when a voltage of around 1 V is applied to read out the resistance value, for example.

As such, second electrode **108** is formed of a metal having a catalytic effect or formed, for example, of platinum, and the region of second electrode **208** where second electrode **208** makes contact with local region **107** is heated by heat generated in local region **107**. This can increase the efficiency of dissociating a hydrogen-containing gas to yield hydrogen atoms. As a result, when there is a hydrogen-containing gas in a gas to be inspected, the hydrogen atoms resulting from the hydrogen-containing gas dissociated by second electrode **108** couple with oxygen atoms within local region **107**, and thus the resistance value of local region **107** decreases.

Gas sensor **100** has a characteristic in which the resistance value of metal oxide layer **106** decreases when second electrode **108** comes into contact with a hydrogen-containing gas through the mechanism described above. With this characteristic, a hydrogen-containing gas included in a gas to be inspected can be detected by bringing the gas to be inspected into contact with second electrode **108** and observing the decrease in the resistance value across first electrode **105** and second electrode **108**.

Regardless of whether local region **107** is in the high-resistance state or the low-resistance state, the resistance value further decreases as a hydrogen-containing gas comes into contact with second electrode **108**. Therefore, a hydrogen-containing gas can be detected by the gas sensor regardless of whether local region **107** is in the high-resistance state or the low-resistance state. However, in order to detect a decrease in the resistance value more clearly, a gas sensor in which local region **107** is set to an electrically high-resistance state in advance may be used.

In the following section, the details of gas sensor **100** for obtaining a stable resistance change characteristic will be described.

An assumption here is that metal oxide layer **106** contains a metal oxide of an oxygen deficit type. For the base metal of the metal oxide, at least one metal may be selected from the group consisting of transition metals such as tantalum, hafnium (Hf), titanium (Ti), zirconium (Zr), niobium (Nb), tungsten (W), nickel (Ni), and iron (Fe) and aluminum (Al). In particular, since transition metals can take a plurality of oxidation states, different resistance states can be achieved through the oxidation-reduction reaction.

In this example, a metal oxide of an oxygen deficit type refers to a metal oxide with an oxygen content (atomic ratio) smaller than that of the composition of the metal oxide having the stoichiometric composition that is normally an insulator. Many metal oxides of an oxygen deficit type behave like a semiconductor in a normal state. The use of a metal oxide of an oxygen deficit type as metal oxide layer **106** makes it possible to achieve a highly reproducible and stable resistance changing operation in gas sensor **100**.

For example, when hafnium oxide is used as the metal oxide contained in metal oxide layer **106**, if x is 1.6 or greater when the composition of the hafnium oxide is expressed as HfO_x, the resistance value of metal oxide layer **106** can be changed stably. In this case, the hafnium oxide may have a film thickness of 3 nm to 4 nm.

Meanwhile, when zirconium oxide is used as the metal oxide contained in metal oxide layer **106**, if x is 1.4 or greater when the composition of the hafnium oxide is expressed as ZrO_x, the resistance value of metal oxide layer **106** can be changed stably. In this case, the zirconium oxide may have a film thickness of 1 nm to 5 nm.

Meanwhile, when tantalum oxide is used as the metal oxide contained in metal oxide layer **106**, if x is 2.1 or greater when the composition of the hafnium oxide is expressed as TaO_x, the resistance value of metal oxide layer **106** can be changed stably.

The compositions of the metal oxide layers illustrated above can be measured by use of the Rutherford backscattering spectrometry.

Materials for first electrode **105** and second electrode **108** may be selected, for example, from platinum, iridium (Ir), palladium (Pd), silver (Ag), nickel, tungsten, copper (Cu), aluminum, tantalum, titanium, titanium nitride (TiN), tantalum nitride (TaN), and titanium aluminum nitride (TiAlN).

Specifically, for the material for second electrode **108**, a material having a catalytic effect of dissociating a gas molecule containing hydrogen atoms into the hydrogen atoms may be used, and examples of such a material may include platinum, iridium, and palladium. Meanwhile, for the material for first electrode **105**, a material having a standard electrode potential lower than that of the metal constituting the metal oxide may be used, and examples of such a material may include tungsten, nickel, tantalum, titanium, aluminum, tantalum nitride, and titanium nitride. In this example, as the standard electrode potential is higher, the material is oxidized less easily.

For substrate **101**, a silicon single crystal substrate or a semiconductor substrate, for example, can be used, but these are not limiting examples. Metal oxide layer **106** can be formed at a relatively low substrate temperature, and therefore metal oxide layer **106** can be formed even on a resin material or the like, for example.

Moreover, gas sensor **100** may further include, for example, a fixed resistance, a transistor, or a diode as a load element electrically connected to metal oxide layer **106**.

Moreover, gas sensor **100** may include a measuring circuit that measures the current that flows in metal oxide layer **106** when a predetermined voltage is applied across first electrode **105** and second electrode **108**. Alternatively, gas sensor **100** may include a power supply circuit that applies a predetermined voltage continuously across first electrode **105** and second electrode **108**. With such a configuration, a highly utilizable gas sensor can be obtained as a module component including a measuring circuit or a power supply circuit.

Method of Manufacturing Gas Sensor

In the following section, an example of a method of manufacturing gas sensor **100** according to the present embodiment will be described with reference to FIGS. **2**A to **2**J, FIG. **3**, and FIG. **4**.

First, as illustrated in FIG. **2**A, aluminum is deposited, for example, on silicon substrate **101** to the thickness of, for example, 400 nm. Then, a wiring pattern is patterned through a photolithography technique, the aluminum is etched through a dry etching technique, and the aluminum is processed into a wiring pattern to form first wiring **102**. At this point, an insulating film formed, for example, through a chemical vapor deposition (CVD) technique may be interposed between first wiring **102** and silicon substrate **101**. First wiring **102** can also be formed of copper, instead of aluminum, or an adhesive layer made of titanium, titanium nitride, or the like, may also be formed on top of and under the aluminum.

Then, a silicon oxide film is deposited on first wiring **102** through, for example, a CVD technique, to the thickness of 500 nm to form second insulating film **103**. In this case, second insulating film **103** may have a layered structure of a silicon oxide film and a silicon nitride film.

Next, a mask patterned into a hole shape is disposed on second insulating film **103** through a photolithography technique, and then a hole penetrating through second insulating film **103** and reaching first wiring **102** is formed by use of the stated mask through a dry etching technique (not illustrated). Thereafter, as illustrated in FIG. **2**B, tungsten is deposited on the entire surface of the wafer to the thickness of 800 nm through a CVD technique, and first contact plug film **104***a* is deposited within the hole so as to be in contact with first wiring **102**. First contact plug film **104***a* may be made of copper, or an adhesive layer and a barrier layer made of titanium, titanium nitride, tantalum, tantalum nitride, or the like can be formed between first contact plug film **104***a* made of tungsten, copper, or the like and first wiring **102** and second insulating film **103**.

Next, as illustrated in FIG. **2**C, first contact plug film **104***a* is polished through a chemical mechanical polishing (CMP) technique to expose second insulating film **103**, and first contact plug **104** is formed inside the hole.

The surface of first contact plug film **104***a* is set to be at least level with or lower than the surface of surrounding second insulating film **103**.

Next, as illustrated in FIG. **2**D, the upper portion of second insulating film **103** is etched, for example, by 50 nm with a chemical liquid containing hydrofluoric acid (HF) through a wet etching technique to allow the surface of the upper portion of first contact plug **104** to project from the surface of second insulating film **103** surrounding first contact plug **104**. In this manner, second step **122** is formed at the border between first contact plug **104** and second insulating film **103**.

Next, as illustrated in FIG. **2**E, as first electrode film **105***a*, a tantalum nitride film having a thickness of, for example, 30 nm is formed so as to cover the surface of second insulating film **103** and the surface of first contact plug **104** projecting from the surface of second insulating film **103** through a sputtering technique. At this point, first electrode film **105***a* may be a laminated film of titanium, titanium nitride, or the like. Next, metal oxide film **106***a* having a thickness of 30 nm is formed on first electrode film **105***a* through a reactive sputtering technique in which, for example, Ta is used as a target. Next, as second electrode film **108***a*, a platinum film having a thickness of, for example, 10 nm is formed on metal oxide film **106***a* through a sputtering technique. In this example, the film thickness of the platinum film is desirably no less than 5 nm nor greater than 200 nm.

Through the above processes, second step **122** between the surface of second insulating film **103** and the surface of first contact plug **104** that is formed so as to project upward from the surface of surrounding second insulating film **103** is transferred to first electrode film **105***a*, metal oxide film **106***a*, and second electrode film **108***a*, and this results in a structure having first step **121** formed on second electrode film **108***a* near the border region between first contact plug **104** and second insulating film **103**.

Next, as illustrated in FIG. **2**F, through, for example, a photolithography technique, first mask **112** composed of photoresist is formed into the shape of the sensor on second electrode film **108***a* that includes first step **121** as viewed in plan view. The dimensions of first mask **112** formed at this point as viewed in plan view may be, for example, from 1 μm on each side to 8 μm on each side.

Next, as illustrated in FIG. **2**G, first electrode film **105***a*, metal oxide film **106***a*, and second electrode film **108***a* are patterned into the shape of the gas detecting element through a dry etching technique in which first mask **112** is used, and thus the gas detecting element including first electrode **105**, metal oxide layer **106**, and second electrode **108** is formed.

Next, as illustrated in FIG. **2**H, as first insulating film **109**, a silicon oxide film having a thickness of, for example, 800 nm is formed so as to cover at least a part of metal oxide layer **106** and a part of second electrode **108**. Thereafter, the upper portion of first insulating film **109** is polished by 300 nm through a CMP technique to flatten the surface of first insulating film **109**. Thereafter, a via hole penetrating through first insulating film **109** and reaching a part of second electrode **108** is formed through an etching technique, tungsten is deposited on the entire surface of the wafer to the thickness of 800 nm through a CVD technique, and then the tungsten is flattened so as to remain only inside the plug through a CMP technique. Thus, second contact plug **110** is formed. Thereafter, another conductive film is deposited on first insulating film **109** and patterned, and thus second wiring **111** connected to second contact plug **110** is formed.

Next, as illustrated in FIG. **2**I, second mask **113** composed of photoresist is formed on first insulating film **109** through a lithography technique. At this point, as viewed in plan view, the opening in second mask **113** is formed into a shape that includes the entirety of first step **121** formed on second electrode **108** within second electrode **108**.

Next, as illustrated in FIG. **2**J, first insulating film **109** is etched by use of second mask **113** through a dry etching technique, and opening **109***a* exposing a part of the surface of second electrode **108** is formed.

Next, as illustrated in FIG. **3**, an initial breakdown voltage is applied across first electrode **105** and second electrode **108** in gas sensor **100** to form local region **107** within metal oxide layer **106**, and thus gas sensor **100** is completed.

As described above, local region **107** is generated concentratedly in metal oxide layer **106** near first step **121** formed as second step **122** formed between first contact plug **104** and second insulating film **103** is transferred onto metal oxide layer **106**. Specifically, local region **107** is generated concentratedly near first step **121** formed on second electrode **108**.

Hydrogen-Containing Gas Reaction Characteristics

First, with regard to one example of the resistance change characteristic associated with the voltage application in gas sensor **100** according to the present embodiment, a result of a measurement by a sample element will be described. The resistance change characteristic of gas sensor **100** caused by a hydrogen-containing gas according to the present embodiment will be described later.

FIG. **4** illustrates a measurement result indicating an example of the resistance change characteristic of gas sensor **100** caused by the voltage application according to the present embodiment.

In gas sensor **100** serving as a sample element, first electrode **105**, second electrode **108**, and metal oxide layer **106** each have dimensions of 3 μm by 3 μm (the area of 9 μm^2). When the composition of the tantalum oxide contained in metal oxide layer **106** is expressed as TaO_y, y is set to 2.47, and the thickness of metal oxide layer **106** is set to 5 nm.

When a read voltage (e.g., 0.4 V) is applied across first electrode **105** and second electrode **108** in gas sensor **100** configured as described above, initial resistance value RI is from about $10^6\Omega$ to $10^9\Omega$.

As illustrated in FIG. **4**, when the resistance value of gas sensor **100** is at initial resistance value RI that is higher than resistance value HR in the high-resistance state, applying the initial breakdown voltage (e.g., 3 V) across first electrode

105 and second electrode 108 causes the resistance value to change to low resistance value LR (step S301).

Next, when two types of voltage pulses, for example, having a pulse duration of 100 ns and having different polarities, or specifically, a positive voltage pulse (e.g., 2.5 V) and a negative voltage pulse (e.g., 1.8 V), are applied as write voltages in an alternating manner across first electrode 105 and second electrode 108 of gas sensor 100, the resistance value of metal oxide layer 106 changes, as illustrated in FIG. 4.

In other words, when a positive voltage pulse is applied across the electrodes as a write voltage, the resistance value of metal oxide layer 106 increases from low resistance value LR to high resistance value HR (step S302). Meanwhile, when a negative voltage pulse is applied across the electrodes as a write voltage, the resistance value of metal oxide layer 106 decreases from high resistance value HR to low resistance value LR (step S303). The polarity of the voltage pulse is defined as being positive when the potential of second electrode 108 is higher than the potential of first electrode 105 or defined as being negative when the potential of second electrode 108 is lower than the potential of first electrode 105.

Utilizing such a resistance change characteristic caused by the voltage application, gas sensor 100 is set to be in the high-resistance state by applying a positive voltage pulse in the end across first electrode 105 and second electrode 108 before starting to monitor a hydrogen-containing gas.

With this initial setting, as described above, any decrease in the resistance value can be detected more clearly than in a case where a hydrogen-containing gas is detected by use of gas sensor 100 in the low-resistance state, and thus the performance of detecting a hydrogen-containing gas improves.

Next, the resistance change characteristic of gas sensor 100 caused by a hydrogen-containing gas according to the present embodiment will be described.

FIG. 5 is a graph illustrating an example of evaluating gas sensor 100 according to the present embodiment. The horizontal axis represents the time (a.u.), and the vertical axis represents the current value (a.u.) of the current that flows between first electrode 105 and second electrode 108.

In the experiment, first, a nitrogen gas was introduced into a closed vessel housing gas sensor 100. Then, the nitrogen gas was switched to a hydrogen gas, and the hydrogen gas was then switched to a nitrogen gas. Gas sensor 100 in which local region 107 was set to the high-resistance state in advance by applying a predetermined voltage across first electrode 105 and second electrode 108 was used.

FIG. 5 illustrates the evaluation result obtained in this experiment, and the horizontal axis indicates three periods: the initial introduction of nitrogen (step S501), the introduction of hydrogen (step S502), and the subsequent introduction of nitrogen (step S503). FIG. 5 reveals that the current value started increasing immediately after the introduced gas was switched from a nitrogen gas to a hydrogen gas. Moreover, FIG. 5 reveals that the current started decreasing immediately after the introduced gas was switched from a hydrogen gas to a nitrogen gas.

In a specific operation of monitoring a hydrogen-containing gas, while a detection voltage of 0.6 V was applied across first electrode 105 and second electrode 108, a current of from 10 μA to 20 μA flowed between first electrode 105 and second electrode 108 when the hydrogen gas was detected. In other words, the experiment reveals that, with gas sensor 100 according to the present embodiment, a hydrogen-containing gas can be monitored with very small power consumption of from 0.006 mW to 0.012 mW.

Based on this result, the inventors speculate as follows concerning the mechanism of detecting a hydrogen gas with gas sensor 100.

First, when a hydrogen-containing gas comes into contact with second electrode 108, the hydrogen-containing gas is dissociated to yield hydrogen atoms through the catalytic effect of second electrode 108. The resulting hydrogen atoms diffuse within second electrode 108 so as to maintain the state of equilibrium and reach local region 107.

Next, these hydrogen atoms cause a reductive reaction of the metal oxide in local region 107, and as oxygen in local region 107 bonds with hydrogen, the degree of oxygen deficiency of the metal oxide included in local region 107 increases. As a result, filaments in local region 107 link together more easily, and the resistance value of local region 107 decreases. Thus, the current that flows between first electrode 105 and second electrode 108 increases.

In contrast, when the hydrogen-containing gas ceases to exist near second electrode 108, hydrogen atoms turn into hydrogen molecules near the surface of second electrode 108 so as to maintain the state of equilibrium and thus move to the outer side from the surface of second electrode 108.

As such, a reaction in which water molecules generated in local region 107 through the previous reductive reaction are decomposed into hydrogen atoms and oxygen atoms occurs, and the hydrogen atoms generated in local region 107 return into second electrode 108. Meanwhile, the oxygen atoms generated in local region 107 bond with oxygen vacancies, and thus the degree of oxygen deficiency of the metal oxide included in local region 107 decreases. As a result, filaments in local region 107 become harder to link together, and the resistance value increases. Thus, the current that flows between first electrode 105 and second electrode 108 decreases.

The operation described above is not limited to gas sensor 100 according to the present embodiment and is considered to occur in a similar manner in a gas sensor of which the structure of the pertinent portions is substantially equal to that of gas sensor 100 according to the present embodiment or in other gas sensors described later.

The operation described above is not limited to a case where the gas that comes into contact with second electrode 108 is a hydrogen gas and is considered to occur in a similar manner even in a case where, for example, the gas that comes into contact with second electrode 108 is a hydrogen-containing gas, such as methane or alcohol.

Next, some advantageous effects of the step formed by first contact plug 104 and second insulating film 103 will be described.

FIG. 6 illustrates a result of comparing the initial breakdown voltage of metal oxide layer 106 between a gas sensor according to a comparative example that is formed through a method similar to that for the gas sensor according to the present embodiment except that no step is formed (referred to below as a no-step gas sensor) and a gas sensor formed according to the present embodiment.

As can be seen clearly from FIG. 6, the initial breakdown voltage is lower in the gas sensor according to the present embodiment. This is due to the following. The step shape formed on first contact plug 104 and second insulating film 103 is transferred to first electrode 105, metal oxide layer 106, and second electrode 108 as well, and thus the electric field is enhanced at this step portion, which causes the

effective voltage applied to metal oxide layer **106** to rise. Therefore, local region **107** is formed selectively near the step portion.

FIG. **7** illustrates the rate of operation of each of the no-step gas sensor and the gas sensor formed according to the present embodiment under the condition in which the concentration of hydrogen in the gas to be detected is, for example, 1%.

As can be seen clearly from FIG. **7**, the rate of operation of the gas sensor formed according to the present embodiment improves more than the rate of operation of the no-step gas sensor. This is possibly because, since there is no step in the no-step gas sensor, local region **107** is formed randomly in the no-step gas sensor and can be formed at a location that is covered by first insulating film **109**, for example. In this case, hydrogen may not reach local region **107**, preventing the gas sensor from operating as a gas sensor. Meanwhile, in the gas sensor formed according to the present embodiment, it is highly likely that local region **107** is selectively formed at the step portion near first contact plug **104**, and opening **109***a* is always formed so as to include the portion directly above first contact plug **104**. Therefore, hydrogen can reach local region **107** via second electrode **108**, and this causes the rate of operation as a gas sensor to improve.

As described thus far, with gas sensor **100** according to the present embodiment, gas sensor **100** does not need to be heated by a heater separately, and a hydrogen-containing gas can be detected stably. Thus, a gas sensor that excels in the power saving performance can be obtained.

Embodiment 2

Configuration of Gas Sensor

As with the gas sensor according to Embodiment 1 described above, a gas sensor according to Embodiment 2 is a gas sensor of a metal-insulator-metal (MIM) structure in which a metal oxide layer serving as an insulating film and metal films are laminated together. This gas sensor can detect, without being heated by a heater, a hydrogen-containing gas by utilizing the self-heat generation and the gas sensitivity in a local region formed within a gas sensitive resistance film. In this example, the term "hydrogen-containing gas" is a collective term for gasses that include molecules containing hydrogen atoms, and examples of such hydrogen-containing gases can include hydrogen, methane, and alcohol.

FIG. **8**A is a cross-sectional view illustrating an example of a configuration of gas sensor **200** according to the present embodiment.

FIG. **8**B is a top view illustrating an example of the configuration of gas sensor **200** according to the present embodiment.

The cross section illustrated in FIG. **8**A corresponds to the cross section cut along the VIIIA-VIIIA' line indicated in FIG. **8**B and viewed in the direction indicated by the arrows.

Gas sensor **200** includes substrate **201**; first wiring **202**; second insulating film **203** disposed on first wiring **202**; first contact plug **204** penetrating through second insulating film **203** and connected to first wiring **202**; first electrode **205**, metal oxide layer **206**, and second electrode **208** formed in this order from a lower side on second insulating film **203** so as to cover first contact plug **204**; first insulating film **209** that covers at least a part of first electrode **205**, a part of metal oxide layer **206**, and a part of second electrode **208**; second contact plug **210** penetrating through first insulating film **209** and connected to second electrode **208**; and second wiring **211** formed on first insulating film **209** so as to connect to second contact plug **210**.

In this example, an upper surface of first contact plug **204** lies lower than an upper surface of second insulating film **203**, and third step **223** is formed by first contact plug **204** and second insulating film **203** adjacent to first contact plug **204**.

As such, first step **221** is formed in first electrode **205**, metal oxide layer **206**, and second electrode **208** over first contact plug **204**, as third step **223** formed by first contact plug **204** and second insulating film **203** adjacent to first contact plug **204** is transferred onto first electrode **205**, metal oxide layer **206**, and second electrode **208**.

Moreover, opening **209***a* is formed in first insulating film **209** over second electrode **208**, and an upper surface of second electrode **208** is exposed through opening **209***a*.

In this example, as illustrated in FIG. **8**B, first step **221** on second electrode **208** is exposed at the bottom of opening **209***a*, and first step **121** is formed as third step **223** formed by first contact plug **204** and second insulating film **203** adjacent to first contact plug **204** is transferred onto second electrode **208**. First step **221** is of a downwardly convex shape. In this example, it is not essential that first step **221** be exposed on the upper surface of second electrode **208**. It suffices that first step **221** be formed at a portion located within opening **209***a*, as viewed in plan view, at an interface between metal oxide layer **206** and second electrode **208**.

Metal oxide layer **206** is a layer whose resistance value changes reversibly in accordance with an electrical signal given across first electrode **205** and second electrode **208**. For example, metal oxide layer **206** transitions reversibly between a high-resistance state and a low-resistance state in accordance with the voltage applied across first electrode **205** and second electrode **208** and the presence or absence of a hydrogen-containing gas in a gas that comes into contact with second electrode **208**.

Local region **207** is present inside metal oxide layer **206**, and local region **207** is in contact with second electrode **208** but is not in contact with first electrode **205**.

In this example, local region **207** is a small region that includes a filament formed of an oxygen vacant site, and the filament functions as an electrically conductive path.

To be more specific, metal oxide layer **206** is formed of a metal oxide, and the degree of oxygen deficiency of a metal oxide included in local region **207** of metal oxide layer **206** is greater than the degree of oxygen deficiency of a metal oxide included in a portion of metal oxide layer **206** other than local region **207**.

The degree of oxygen deficiency of the metal oxide included in local region **207** changes reversibly in accordance with the voltage applied across first electrode **205** and second electrode **208** and the presence or absence of a hydrogen-containing gas in a gas that comes into contact with second electrode **208** via opening **209***a*.

Gas sensor **200** configured as described above can provide the following advantageous effects.

As an initial breakdown voltage is applied, local region **207** that is in contact with second electrode **208** but is not in contact with first electrode **205** is formed within metal oxide layer **206**, as illustrated in FIG. **8**A.

In this example, as in Embodiment 1, local region **207** is produced so as to be concentrated in a portion near first step **221** on metal oxide layer **206**, where first step **221** is formed as third step **223** formed between first contact plug **204** and second insulating film **203** is transferred onto metal oxide layer **206**.

This is because when the initial breakdown voltage is applied across first electrode **205** and second electrode **208**, the electric field is enhanced near the step on metal oxide layer **206** and thus local region **207** is formed more easily particularly in the region near this step.

Meanwhile, since first contact plug **204** is formed within opening **209***a* as viewed in plan view, the hydrogen atoms originating from the hydrogen-containing gas dissociated by second electrode **208** reach local region **207** in a short period of time, and thus a gas sensor that excels in the responsiveness can be obtained.

The phenomenon of the resistance change and the mechanism of detecting hydrogen in gas sensor **200** are similar to the phenomenon of the resistance change and the mechanism of detecting hydrogen in gas sensor **100** according to Embodiment 1, and thus repetitive descriptions thereof will be omitted herein.

Method of Manufacturing Gas Sensor

In the following section, an example of a method of manufacturing gas sensor **200** according to the present embodiment will be described with reference to FIGS. **9**A to **9**J and FIG. **10**.

First, as illustrated in FIG. **9**A, aluminum is deposited, for example, on silicon substrate **201** to the thickness of, for example, 400 nm. Then, a wiring pattern is patterned through a photolithography technique, the aluminum is etched through a dry etching technique, and the aluminum is processed into a wiring pattern to form first wiring **202**. At this point, an insulating film formed, for example, through a CVD technique may be interposed between first wiring **202** and silicon substrate **201**. First wiring **202** can also be formed of copper, instead of aluminum, or an adhesive layer made of titanium, titanium nitride, or the like, may also be formed on top of and under the aluminum.

Then, a silicon oxide film is deposited on first wiring **202** through, for example, a CVD technique, to the thickness of 500 nm to form second insulating film **203**. In this case, second insulating film **203** may have a layered structure of a silicon oxide film and a silicon nitride film.

Next, a mask patterned into a hole shape is disposed on second insulating film **203** through a photolithography technique, and then a hole penetrating through second insulating film **203** and reaching first wiring **202** is formed by use of the stated mask through a dry etching technique (not illustrated). Thereafter, as illustrated in FIG. **9**B, tungsten is deposited on the entire surface of the wafer to the thickness of 800 nm through a CVD technique, and first contact plug film **204***a* is deposited within the hole so as to be in contact with first wiring **202**. First contact plug film **204***a* may be made of copper, or an adhesive layer and a barrier layer made of titanium, titanium nitride, tantalum, tantalum nitride, or the like can be formed between first contact plug film **204***a* made of tungsten, copper, or the like and first wiring **202** and second insulating film **203**.

Next, as illustrated in FIG. **9**C, first contact plug film **204***a* is polished through a CMP technique to expose second insulating film **203**, and first contact plug **204** is formed inside the hole.

The surface of first contact plug film **204***a* is set to be at least level with or lower than the surface of surrounding second insulating film **203**.

Next, as illustrated in FIG. **9**D, W is etched, for example, by 30 nm through a dry etching technique, and the surface of the upper portion of first contact plug **204** is formed so as to lie lower than the surface of second insulating film **203** surrounding first contact plug **204**. In this manner, as with the gas sensor according to Embodiment 1, third step **223** is formed at the border between first contact plug **204** and second insulating film **203**. What differs from Embodiment 1 is that third step **223** is formed without etching second insulating film **203** having a large surface area.

Next, as illustrated in FIG. **9**E, as first electrode film **205***a*, a tantalum nitride film having a thickness of, for example, 30 nm is formed so as to cover the surface of second insulating film **203** and the surface of first contact plug **204** recessed from the surface of second insulating film **203** through a sputtering technique. At this point, first electrode film **205***a* may be a laminated film of titanium, titanium nitride, or the like. Next, metal oxide film **206***a* having a thickness of 30 nm is formed on first electrode film **205***a* through a reactive sputtering technique in which, for example, tantalum is used as a target. Next, as second electrode film **208***a*, a platinum film having a thickness of, for example, 10 nm is formed on metal oxide film **206***a* through a sputtering technique. In this example, the film thickness of the platinum film is desirably no less than 5 nm nor greater than 200 nm.

Through the above processes, third step **223** between the surface of second insulating film **203** and the surface of first contact plug **204** formed so as to be recessed downward from the surface of surrounding second insulating film **203** is transferred to first electrode film **205***a*, metal oxide film **206***a*, and second electrode film **208***a*, and this results in a structure having first step **221** formed on second electrode film **208***a* near the border region between first contact plug **204** and second insulating film **203**.

Next, as illustrated in FIG. **9**F, through, for example, a photolithography technique, first mask **212** composed of photoresist is formed into the shape of the sensor on second electrode film **208***a* that includes first step **221** as viewed in plan view. The dimensions of first mask **212** formed at this point may be, for example, from 1 μm on each side to 8 μm on each side.

Next, as illustrated in FIG. **9**G, first electrode film **205***a*, metal oxide film **206***a*, and second electrode film **208***a* are patterned into the shape of the gas detecting element through a dry etching technique in which first mask **212** is used, and thus the gas detecting element including first electrode **205**, metal oxide layer **206**, and second electrode **208** is formed.

Next, as illustrated in FIG. **9**H, as first insulating film **209**, a silicon oxide film having a thickness of, for example, 800 nm is formed so as to cover at least a part of metal oxide layer **206** and a part of second electrode **208**. Thereafter, the upper portion of first insulating film **209** is polished by 300 nm through a CMP technique to flatten the surface of first insulating film **209**. Thereafter, a via hole penetrating through first insulating film **209** and reaching a part of second electrode **208** is formed through an etching technique, tungsten is deposited on the entire surface of the wafer to the thickness of 800 nm through a CVD technique, and then the tungsten is flattened so as to remain only inside the plug through a CMP technique. Thus, second contact plug **210** is formed. Thereafter, another conductive film is deposited on first insulating film **209** and patterned, and thus second wiring **211** connected to second contact plug **210** is formed.

Next, as illustrated in FIG. **9**I, second mask **213** composed of photoresist is formed on first insulating film **209** through a lithography technique. At this point, as viewed in plan view, the opening in second mask **213** is formed into a shape that includes the entirety of first step **221** formed on second electrode **208** within second electrode **208**.

Next, as illustrated in FIG. **9**J, first insulating film **209** is etched by use of second mask **213** through a dry etching

technique, and opening **209***a* exposing a part of the surface of second electrode **208** is formed.

Next, as illustrated in FIG. **10**, an initial breakdown voltage is applied across first electrode **205** and second electrode **208** in gas sensor **200** to form local region **207** within metal oxide layer **206**, and thus gas sensor **200** is completed.

As described above, local region **207** is generated concentratedly in metal oxide layer **206** near first step **221** formed as third step **223** formed between first contact plug **204** and second insulating film **203** is transferred onto metal oxide layer **206**. Specifically, local region **207** is generated concentratedly near first step **221** formed on second electrode **208**.

The resistance change characteristic associated with the voltage application in gas sensor **200** configured as described above is similar to the resistance change characteristic associated with the voltage application in gas sensor **100** described with reference to FIGS. **4** and **5**.

Moreover, with regard to the mechanism of the resistance change in gas sensor **200** caused by a hydrogen-containing gas as well, the resistance change occurs by a hydrogen-containing gas through a mechanism similar to the mechanism described regarding gas sensor **100**.

As described thus far, with gas sensor **200** according to the present embodiment, gas sensor **200** does not need to be heated by a heater separately, and a hydrogen-containing gas can be detected stably. Thus, a gas sensor that excels in the power saving performance can be obtained.

Embodiment 3

A fuel cell vehicle according to Embodiment 3 includes any one of the gas sensors described above according to Embodiment 1, Embodiment 2, and their variations and detects a hydrogen gas inside the vehicle by use of that gas sensor.

FIG. **11** is a side view illustrating an example of a configuration of fuel cell vehicle **800** according to Embodiment 3.

Fuel cell vehicle **800** includes passenger compartment **810**, luggage compartment **820**, gas tank compartment **830**, fuel tank **831**, gas sensor **832**, pipe **840**, fuel cell compartment **850**, fuel cell **851**, gas sensor **852**, motor compartment **860**, and motor **861**.

Fuel tank **831** is provided inside gas tank compartment **830** and holds a hydrogen gas as a fuel gas. In this example, gas sensor **832** detects a fuel gas leakage in gas tank compartment **830**.

Fuel cell **851** includes a fuel cell stack in which a plurality of cells serving as base units having a fuel pole, an air pole, and an electrolyte are stacked on top of each other. Fuel cell **851** is provided inside fuel cell compartment **850**. The hydrogen gas inside fuel tank **831** is fed to fuel cell **851** inside fuel cell compartment **850** via pipe **840**. This hydrogen gas and an oxygen gas in the atmospheric air are made to react inside fuel cell **851**, and thus electricity is generated. In this example, gas sensor **852** detects a hydrogen gas leakage in fuel cell compartment **850**.

Motor **861** is provided inside motor compartment **860**. Fuel cell vehicle **800** runs as motor **861** rotates on the power generated by fuel cell **851**. As described above, in one example, a gas sensor according to the present disclosure can detect a hydrogen-containing gas with very small power consumption of around 0.01 mW. Therefore, by utilizing this excellent power saving performance of the gas sensor, a hydrogen gas leakage can be monitored continuously without a large increase in the standby power of the fuel cell vehicle.

For example, a predetermined voltage may be applied continuously to each of gas sensor **832** and gas sensor **852** regardless of the operation state of the ignition key in fuel cell vehicle **800**, and whether any hydrogen gas is present outside fuel tank **831** in gas tank compartment **830** and outside fuel cell **851** in fuel cell compartment **850** may be determined based on the amount of the current that flows in each of gas sensor **832** and gas sensor **852**.

With this configuration, for example, since the presence or absence of a hydrogen gas leakage has already been determined when the ignition key is operated, the time it takes to start the fuel cell vehicle can be reduced as compared to a case where a gas sensor is driven to determine the presence or absence of a hydrogen gas leakage after the ignition key has been operated. Moreover, the above configuration can continue to monitor a hydrogen gas leakage, for example, even after the fuel cell vehicle has been stored into a garage after having been driven. Thus, the safety can be improved.

Thus far, a gas sensor, a method of detecting a hydrogen gas, and a fuel cell vehicle according to some aspects of the present disclosure have been described based on some embodiments, but the present disclosure is not limited to these embodiments. Unless departing from the spirit of the present disclosure, an embodiment obtained by making various modifications that are conceivable by a person skilled in the art to the present embodiments or an embodiment obtained by combining constituent elements in the foregoing embodiments is also encompassed by the scope of the present disclosure.

For example, the gas sensor described above may further include a measuring circuit that measures the current that flows in a metal oxide layer when a predetermined voltage is applied across a first electrode and a second electrode.

Moreover, the gas sensor described above may further include a power supply circuit that applies a predetermined voltage continuously across a first electrode and a second electrode.

With such a configuration, a highly utilizable gas sensor can be obtained as a module component including a measuring circuit or a power supply circuit.

Although only some exemplary embodiments of the present disclosure have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of the present disclosure. Accordingly, all such modifications are intended to be included within the scope of the present disclosure.

INDUSTRIAL APPLICABILITY

A gas sensor according to the present disclosure functions as a gas sensor that excels in the power saving performance and finds its effective use as a hydrogen sensor used in a fuel cell vehicle or the like, for example.

The invention claimed is:

1. A gas sensor, comprising:

a gas detecting element that includes a first electrode, a metal oxide layer provided on the first electrode, and a second electrode provided on the metal oxide layer, the gas detecting element detecting a gas molecule existing in a gas and including a hydrogen atom; and

a first insulating film having an opening that allows a part of the second electrode to be exposed therethrough, the

first insulating film covering the first electrode, the metal oxide layer, and another part of the second electrode, wherein

the metal oxide layer has a characteristic in which a resistance value of the metal oxide layer changes when the second electrode comes into contact with the gas molecule,

a first step is provided at a portion lying on an interface between the metal oxide layer and the second electrode and located within the opening as viewed in plan view,

a local region is provided in the metal oxide layer and close to the first step,

a degree of oxygen deficiency of the local region is greater than a degree of oxygen deficiency of a region other than the local region in the metal oxide layer, and

in the plan view, the first electrode is larger than the first step.

2. The gas sensor according to claim **1**, wherein

the first step is of an upwardly convex shape.

3. The gas sensor according to claim **2**, further comprising:

a first contact plug provided between a substrate and the first electrode, wherein

the first contact plug includes a side surface surrounding the first contact plug, and the side surface is covered by a second insulating film,

the first contact plug has an upper surface that projects from an upper surface of the second insulating film,

the first electrode includes a second step provided across the upper surface of the first contact plug and the upper surface of the second insulating film surrounding the first contact plug, and

the first step is a step resulting from a transfer of the second step onto an upper surface of the metal oxide layer.

4. The gas sensor according to claim **1**, wherein

the first step is of a downwardly convex shape.

5. The gas sensor according to claim **4**, further comprising:

a first contact plug provided between a substrate and the first electrode, wherein

a side surface surrounding the first contact plug is covered by a second insulating film,

an upper surface of the first contact plug is recessed from an upper surface of the second insulating film,

the first electrode includes a third step provided across the upper surface of the first contact plug and the upper surface of the second insulating film surrounding the first contact plug, and

the first step is a step resulting from a transfer of the third step onto an upper surface of the metal oxide layer.

6. The gas sensor according to claim **1**, wherein

the second electrode includes a material having a catalytic effect of dissociating the gas molecule into the hydrogen atom.

7. The gas sensor according to claim **6**, wherein

the second electrode includes platinum or palladium.

8. The gas sensor according to claim **1**, wherein

the metal oxide layer transitions reversibly between a high-resistance state and a low-resistance state in accordance with a voltage applied across the first electrode and the second electrode.

9. The gas sensor according to claim **1**, further comprising:

a current detector that detects a current that flows in the metal oxide layer when a predetermined voltage is applied across the first electrode and the second electrode, wherein

a decrease in the resistance value is detected based on an increase in the current detected by the current detector.

10. The gas sensor according to claim **1**, wherein

the metal oxide layer includes a transition metal oxide.

11. The gas sensor according to claim **10**, wherein

the transition metal oxide is any one of tantalum oxide, hafnium oxide, or zirconium oxide.

12. The gas sensor according to claim **1**, further comprising:

a second contact plug penetrating through a part of a portion of the first insulating film where the first insulating film covers the second electrode and connected to the second electrode; and

a conductor connected to the second contact plug at an upper side of the second contact plug.

13. A fuel cell vehicle, comprising:

a passenger compartment;

a gas tank compartment housing a hydrogen gas tank;

a fuel cell compartment housing a fuel cell; and

the gas sensor according to claim **1**, wherein

the gas sensor is provided in at least one of the gas tank compartment or the fuel cell compartment.

* * * * *